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NUMBER 1

THE EFFECTS OF TROPOSPHERIC AND STRATOSPHERIC ADVECTION ON PRESSURE AND TEMPERATURE VARIATIONS¹

By C. M. PENNER²

Abstract

Pressure and temperature variations at Sault Ste. Marie during 1938-39 for all levels up to 20 km. have been studied. The pressure extremes are progressively retarded at higher levels in the troposphere, while in the stratosphere the retardation decreases so that the phase becomes more nearly that of the surface pressure. The temperature extremes at greater altitudes in the troposphere are advanced with respect to the surface values. In the stratosphere the temperature variation reverses phase. Pressure and temperature anomalies are discussed in their relation to advection. High surface pressures are accompanied by a warm troposphere and a cold stratosphere. The opposite is true of low surface pressures. Seasonal differences in pressure and temperature variations are discussed.

Introduction

One of the fundamental problems of synoptic as well as dynamic meteorology is the determination of the causes of pressure and temperature variations and the discovery of the underlying physical processes. With the increasing use of aerological observations for daily forecasting, a clear understanding of the interactions between the different atmospheric strata is becoming more and more valuable.

Correlation studies of upper air data were first made by W. H. Dines (3, p. 271) and A. Schedler (8). From an investigation of interdiurnal pressure and temperature variations, Schedler (9) concluded that the stratosphere is of major importance as compared to the troposphere in bringing about surface pressure variations. Later results (4) indicated that the troposphere is, at least, equally effective in causing surface pressure variations. Further studies of interdiurnal variations of the pressure and temperature (4, 5, 6, 9) showed that the extreme values of the pressure take place in the rear of lows and highs at greater altitudes up to 8 km. The extreme values of the temperature are displaced forward, at higher levels in the troposphere, with respect to the surface values. It is the purpose of the present investigation to extend these studies to greater heights, well up into the stratosphere.

To this end, the radiosonde observations taken at Sault Ste. Marie, Mich., during 1938-39 are analyzed. The data are arranged in six groups according to the position of Sault Ste. Marie, relative to surface pressure systems (i.e.,

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highs and lows). Sault Ste. Marie must be situated in one of the following six areas:—

Lf—front or east side of a low.

Lc—centre of a low.

Lr—rear or west side of a low.

Hf—front or east side of a high.

Hc—centre of a high.

Hr—rear or west side of a high.

Since almost all pressure systems move from west to east, the east side can be called the front and the west side the rear. To decide into which area Sault Ste. Marie belonged at a given time, the daily weather maps of the Canadian Meteorological Service were used. The position of the station is, naturally, somewhat arbitrary since no fixed rules can be given as to what should constitute the boundaries of the above areas. The term centre has been applied, generally, to the innermost two or three isobars, but as the horizontal extent of the pressure systems is extremely variable, each case must be considered individually without any attempt to apply general rules.

Mean values of the pressures and temperature in each area have been found for every 2 km. level from the surface to 20 km. The values are plotted, arranging the six areas, into which the highs and lows have been divided, on an idealized time axis in the sequence given above. The curves are fairly regular. They were therefore subjected to a harmonic analysis. Further, the observations have been divided according to seasons, summer and winter, and the mean values have been calculated separately for each season.

Variations of Pressure and Temperature at the Different Levels during the Passage of Highs and Lows at the Surface

Harmonic Analysis; Pressure and Temperature Variations

The number of observations at some of the levels and in each area is given in Table I. The number is sufficient to form a fairly reliable statistical mean at all heights except 20 km., where much fewer observations are available than at 18 km.

TABLE I
NUMBER OF OBSERVATIONS IN THE DIFFERENT AREAS AND AT EACH LEVEL

Height, km.	0	10	18	Height, km.	0	10	18
Area				Area			
<i>Lf</i>	61	53	25	<i>Hc</i>	70	67	25
<i>Lc</i>	42	36	11	<i>Hr</i>	53	48	22
<i>Lr</i>	60	48	15				
<i>Hf</i>	74	68	17	Total	360	320	115

In Table II are found the mean values of P_z and T_z , the pressure and temperature at a level z , the height of the tropopause H , and the pressure P_H and the temperature T_H at the tropopause, for all data.

The mean values of P_z , T_z , P_H , and T_H for all the data at every level in each area have been plotted in Figs. 1 and 2. Since the curves are quite regular, they have been expressed by a trigonometric series of the form $A_1 \cos(t - \alpha_1) + A_2 \cos(2t - \alpha_2)$. For the purpose of the harmonic analysis

TABLE II
MEAN VALUES OF P_z , T_z , P_H , T_H , AND H FOR ALL DATA

$P_0 = 987.0$ mb.	$T_0 = +3.3^\circ \text{C.}$	$P_{12} = 194.8$ mb.	$T_{12} = -54.1^\circ \text{C.}$
$P_2 = 791.9$	$T_2 = -0.8$	$P_{14} = 142.8$	$T_{14} = -56.7$
$P_4 = 613.7$	$T_4 = -10.8$	$P_{16} = 104.3$	$T_{16} = -59.2$
$P_6 = 470.3$	$T_6 = -23.1$	$P_{18} = 76.7$	$T_{18} = -59.4$
$P_8 = 355.1$	$T_8 = -36.8$	$P_{20} = 55.1$	$T_{20} = -58.4$
$P_{10} = 264.3$	$T_{10} = -48.1$	$P_H = 229.2$	$T_H = -57.6$
$H = 11.15$ km.			

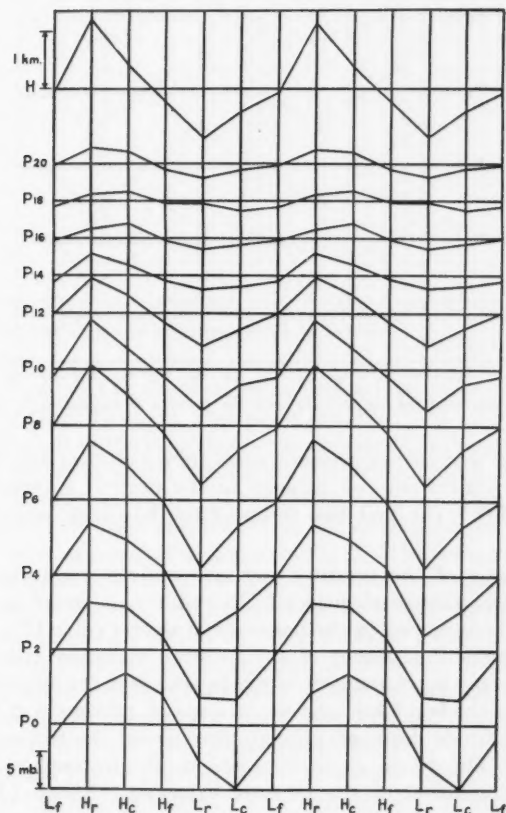


FIG. 1. Variation of the pressure and of the height of the tropopause with the passage of surface highs and lows; yearly mean.

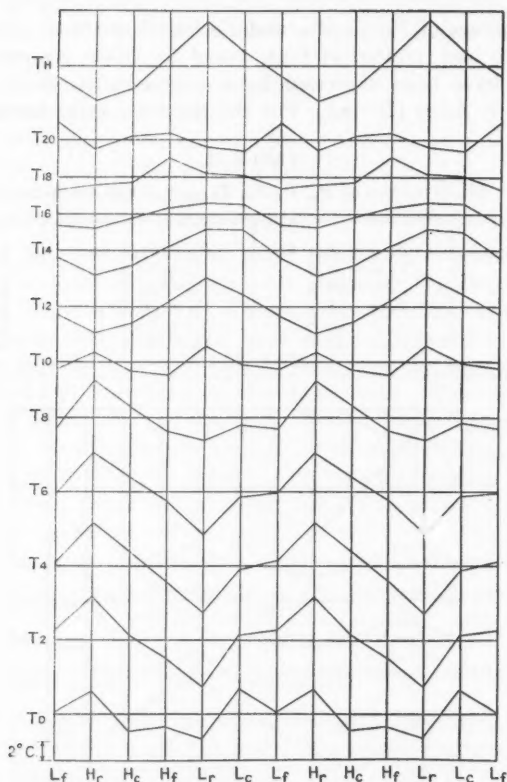


FIG. 2. Variation of the temperature with the passage of surface highs and lows; yearly mean.

it was assumed that the six pressure areas are equidistant and that one cycle comprises the time from one passage to the next of a certain region (L_f . . . H_r , L_f). The first two terms of the harmonic series are given in Table III.

The behaviour of the pressure and temperature variations at different levels during the passage of surface highs and lows is shown in Figs. 1 and 2 and is clearly brought out by the harmonic analysis (Table III). Considering the first harmonic component of the pressure variation (the second component is generally much smaller), it can be seen that the amplitude decreases only slightly in the first 4 km. and shows a second maximum at 6 km. Above 6 km. the amplitude decreases strongly throughout the troposphere and the stratosphere. The phase angle increases in the troposphere, showing the progressive retardation of the pressure extremes. Above 12 km. (in the stratosphere) the retardation decreases and at 18 km. the phase is again nearly equal to that of the surface pressure. This shows that the retardation

TABLE III
HARMONIC COMPONENTS OF THE PRESSURES AND TEMPERATURES DURING THE PASSAGE
OF SURFACE HIGHS AND LOWS—YEARLY MEAN

—	A_1 , mb.	α_1 , °	A_2 , mb.	α_2 , °
P_0	7.8	247	1.1	343
P_2	7.4	264	0.3	332
P_4	7.0	274	0.6	33
P_6	7.4	281	0.7	105
P_8	6.9	284	0.6	165
P_{10}	5.0	284	1.0	190
P_{12}	4.1	287	0.6	180
P_{14}	2.2	277	0.8	204
P_{16}	1.5	269	0.4	132
P_{18}	1.1	249	0.5	210
P_{20}	1.8	283	0.5	153
H	0.88 km.	288	0.19 km.	212
T_0	2.1° C.	356	0.6° C.	153
T_2	3.8	313	0.6	134
T_4	3.9	300	0.7	132
T_6	3.5	294	0.7	143
T_8	2.5	289	1.2	196
T_{10}	0.4	64	1.5	230
T_{12}	2.8	111	0.2	232
T_{14}	2.6	104	0.3	125
T_{16}	1.5	126	0.4	133
T_{18}	1.4	155	0.4	0
T_{20}	0.4	283	1.3	11
T_H	4.0	113	0.6	263

of the pressure extremes continues only in the troposphere and that the retardation decreases in the stratosphere.

From the first harmonic component of the temperature series, it is seen that the amplitude of the temperature variation increases from 0 to 4 km.; then it decreases rapidly as the tropopause is approached. At 10 km., which is roughly the height of the tropopause, the amplitude of the second harmonic component of the temperature variation is about four times as great as the amplitude of the first harmonic. Thus the temperature variation at 10 km. during the passage of highs and lows does not resemble a simple but rather a double sine curve, as can also be seen from Fig. 2. This anomalous behaviour of the temperature variation in the neighbourhood of the tropopause probably takes place because the temperature variation at 10 km. sometimes is under the influence of stratospheric and at other times of tropospheric advection of air. Above the tropopause the amplitude A_1 increases somewhat, at first, but then it decreases rapidly with height. Thus the maximum temperature variation occurs in the troposphere from 2 to 6 km. and in the lower stratosphere from 12 to 14 km. The phase angle decreases in the troposphere, indicating that the temperature extremes at greater altitudes are advanced with respect to the surface values. Above 10 km. (in the stratosphere) the temperature series have almost exactly the opposite phase. This change in phase of the temperature variation at the tropopause can be explained by

assuming simultaneous advection in the troposphere and in the stratosphere from the same direction. In the troposphere the temperature decreases from S to N, while in the stratosphere the temperature increases from S to N. Hence, advection from the south, for example, would make the troposphere warmer and the stratosphere colder. Thus, where the warmest temperatures occur in the troposphere (i.e., where advection has taken place from the south), the coldest temperatures will be found in the stratosphere. Investigations of aerological ascents in individual cases (7) have shown that when advection from the south takes place (i.e., tropical air replaces polar air) the troposphere becomes warmer and the stratosphere becomes colder and vice versa.

The change in phase of the temperature variation at the tropopause could also be explained by vertical motions, if the assumption is made that where descending currents are found in the stratosphere there are ascending currents in the troposphere, since air is warmed by descent and cooled by ascent. Previous investigations have produced some evidence in support of this theory (7). We shall return to this question later (p. 12).

Two different theories account equally well for the retardation of the pressure extremes in the troposphere. One advanced by Stüve (10) assumes that the surface pressure centres are steered by the pressure distribution aloft. It is known as the theory of "stratospheric steering". The other, the polar front theory, advanced by V. Bjerknes and others (1), considers the lower layers as the primary cause of surface pressure variations and the influence of the upper layers as producing more secondary effects. A brief discussion of both theories is given by Haurwitz and Haurwitz (6).

The retardation of the pressure extremes follows partly as a result of the advance of the temperature extremes, according to the barometric formula. At the surface, the highest pressure and lowest temperature occur over H_c . At higher levels in the troposphere the temperature extremes are advanced, the highest temperature occurring over H_r and the lowest over L_r . Therefore the decrease in pressure with height will be less over H_r than over H_c , for instance. Thus, at higher levels in the troposphere, the highest pressure will tend to occur over H_r rather than over H_c , that is, the pressure extremes will be retarded with respect to the surface values. In the stratosphere, however, the temperature has the opposite phase; the coldest temperatures now are found over H_r and the warmest over L_r . Hence the decrease in pressure with height will now be greater over H_r than over H_f or H_c since the colder air is found over H_r . Consequently, the maximum pressure will again tend to occur over H_c , that is, in the stratosphere the retardation of the pressure extremes becomes less. Similar considerations apply, of course, to minimum pressures.

The forward displacement of the temperature extremes with altitude in the troposphere can probably be explained by higher wind velocities aloft. The increase in wind velocity with height is greatest in the lowest layers. This

agrees with the result that the phase advance is largest in the lowest levels, being 43° in the first 2 km. and 13° from 2 to 4 km. (Table III).

Similar series have been found for the height of the tropopause H , and its temperature T_H . The results confirm previous investigations. The tropopause is lowest in the rear of a surface low and highest in the rear of surface high. A low tropopause is accompanied by a warm stratosphere, a high tropopause by a cold stratosphere.

Temperature and Pressure Anomalies

When the mean temperature for each level and in each area is subtracted from the mean temperature for all data at each level given in Table II, temperature anomalies are obtained. By drawing lines of equal temperature anomaly, the regions of air warmer (positive temperature anomaly) and the regions of air colder (negative temperature anomaly) than normal are indicated. This diagram is shown in Fig. 3. The heavy line is the tropopause. Temperatures lower than normal in the troposphere, in general, are accompanied by temperatures higher than normal in the stratosphere and vice versa. The greatest deviations from the normal occur in the rear of surface highs and lows both in the stratosphere and in the troposphere, temperatures being lower than normal in the rear of a low and higher than normal in the rear of a high in the troposphere. In the stratosphere, temperatures are lower than normal in the rear of a high and higher than normal in the rear of a low. It can be seen that, on the average, advection in the troposphere and the stratosphere from the same direction must produce opposite effects on the surface pressure variation. According to the geostrophic law, the wind blows from a southerly direction on the west side of a high and on the east side of a low. In the rear of a high the air has come from the most southerly latitude, owing to the greater horizontal extent of highs; hence in the troposphere the warmest temperatures and the greatest temperature anomalies would be found over Hr , except in the lowest levels where the effect of the cyclonic warm sector causes the warmest temperatures to be found over Lc . In the stratosphere, advection from the south brings colder air, so that the coldest temperatures and the greatest negative temperature anomaly would be found over Hr . The coldest temperatures in the troposphere occur over Lr following the influx of polar air behind the cold front and before the descending currents found in highs have resulted in the consequent warming of the tropospheric air.

A similar attempt was made to draw lines of equal pressure anomaly. Because of the rapid decrease of the pressure with height, the pressure anomalies at different altitudes are not directly comparable with one another. The pressure at a height z is given by

$$P_z = P_s e^{\frac{-\rho g z}{P_s}}$$

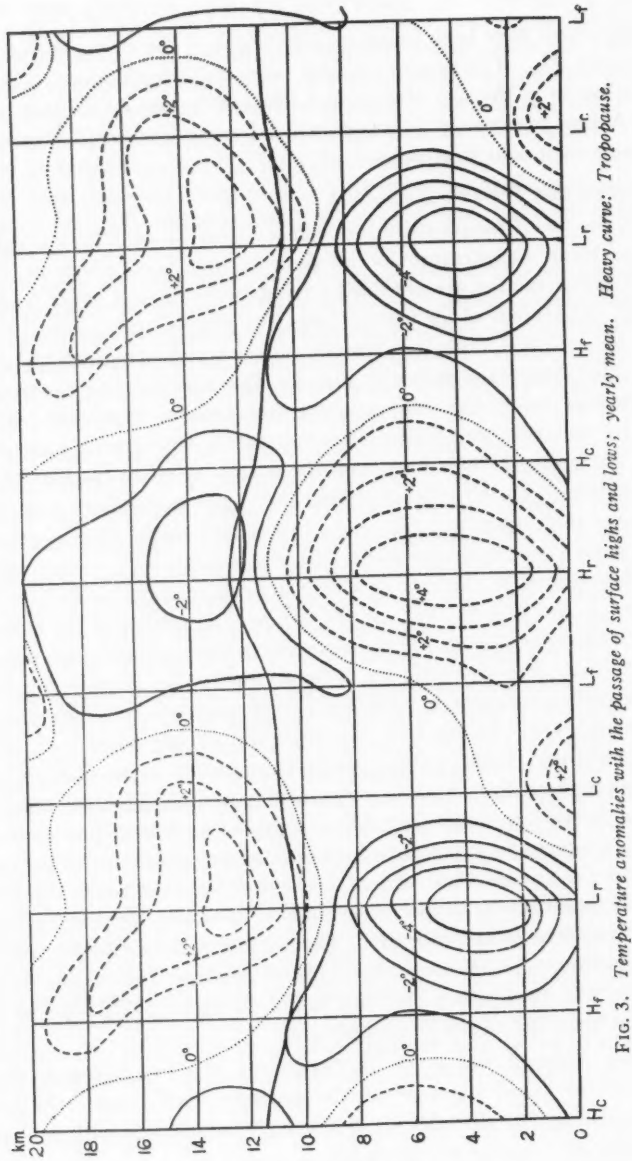


FIG. 3. Temperature anomalies with the passage of surface highs and lows; yearly mean. Heavy curve: Tropopause.

where P_o is the pressure at the surface, g the acceleration of gravity, R the gas constant, and T the mean temperature of the air column. It follows that

$$\frac{dP_o}{P_o} = \frac{dP_z}{P_z} - \frac{gzdT}{RT^2}.$$

Assuming that the temperature of the intermediate layers does not change

$$dP_o = \frac{P_o}{P_z} \times dP_z.$$

Thus, a change dP_o in the surface pressure is P_o/P_z times as large as the pressure change dP_z at a level z . This does not imply, however, that a change dP_z at a level z causes a change P_o/P_z times as great at the surface, since no account has been taken of the compressibility and the possible temperature changes of the air column. For example, if the total advection takes place above the level z , dP_z will represent the mass added above the level z , while dP_o will represent the total mass added to the air column. It would seem, at first, that these two values should be equal. However, if the mass is added above z , the air column below z will be compressed, so that part of the air previously above z will now be below it. dP_z will then represent the total mass of the air added less the mass of the air that sinks below z . dP_o , which represents the total mass added, must be larger than dP_z . Therefore, to make the pressure anomalies more comparable to one another they were multiplied by the factor P_o/P_z . Fig. 4 shows the lines of equal pressure anomaly treated in this manner. The heavy line in the diagram is the position of the tropopause. At the surface the maximum pressure anomalies occur, of course, in the centre of lows and highs. Above 2 km., the largest pressure anomalies are

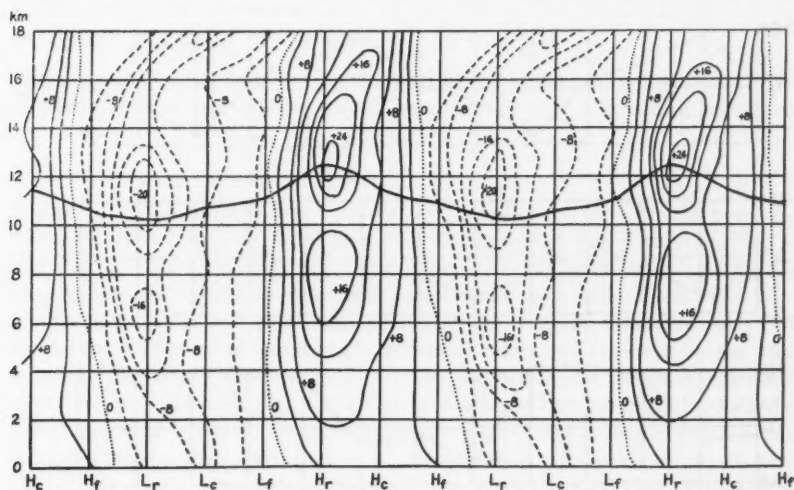


FIG. 4. Reduced pressure anomalies with the passage of surface highs and lows; yearly mean. Heavy curve: Tropopause.

found over the rear of surface lows and highs, with a maximum between 4 and 8 km. altitude and a second maximum in the stratosphere from 10 to 14 km. Above 14 km., the maximum pressure anomalies occur more nearly over L_c and H_c , indicating that the retardation of the pressure extremes becomes less in the stratosphere. In the troposphere, regions where the pressure is below normal are also regions where the temperature is below normal except in the first 3 or 4 km. over L_c where the temperature is above normal. This is the region of the cyclonic warm sector, which does not seem to extend above 4 km. on the average. In the stratosphere, regions where the pressure is below normal are regions where the temperature is above normal.

Advective Changes of Mass

The difference in pressure between any two levels is a measure of the mass between those two levels. In Fig. 5 are plotted the pressure differences for the layer 0-4 km., 4-8 km., 8-12 km., and above 12 km. for each of the six areas of highs and lows. The amplitudes of these curves indicate the amount

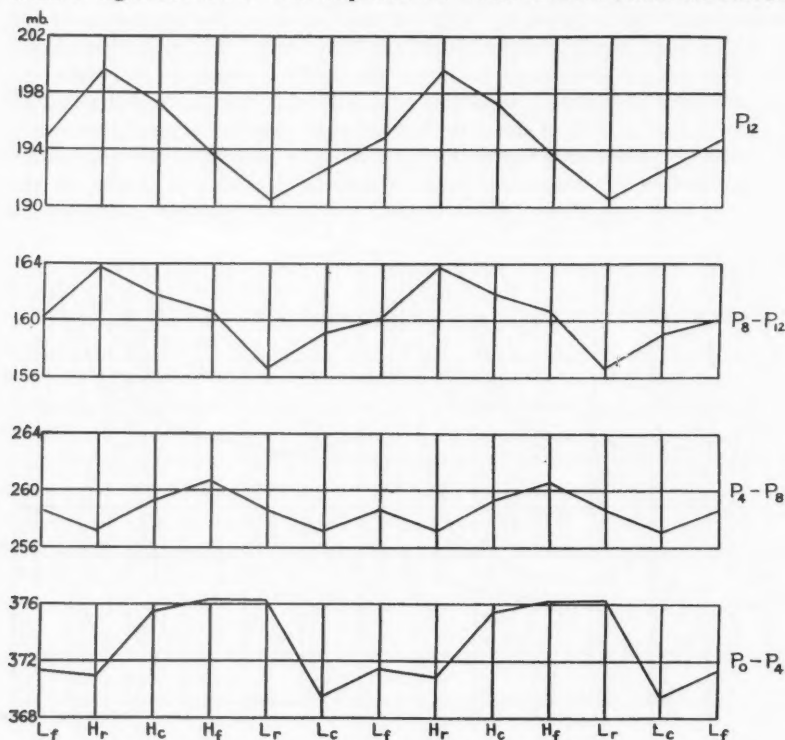


FIG. 5. Variation of mass in different atmospheric layers with the passage of surface highs and lows; yearly mean.

of advective change of mass during the passage of surface highs and lows. Thus, it can be seen that the advective change of mass is greatest in the layer 0-4 km. Here the amplitude is 4.5 mb. In the intermediate layer, 4-8 km. (the upper troposphere), the amplitude is much less, being only 1.8 mb., while in the neighbourhood of the tropopause and in the lower stratosphere (8-12 km.) the amplitude of the advective change of mass is again considerably larger, having increased to 3.5 mb. The amplitude of the advective change of mass at all levels above 12 km. is 4.1 mb. Thus since the surface pressure change is a measure of the total mass added in the atmosphere, it can be seen that the layers in the lower troposphere and in the lower stratosphere are the most important in causing surface pressure variations, while the intermediate layer (the upper troposphere) is much less effective. Previous investigations (6) have shown that the greatest advective changes of mass occur near the surface and near the tropopause. In the lowest layer (0-4 km.) the most pronounced advective change occurs from *Lc* to *Lr*, namely, with the passage of the cold front. In the higher layers the advective changes from one region to the next are approximately of the same order of magnitude for all regions. In the layer 0-4 km. the greatest mass is found over *Lr* and *Hf* where advection from the N has occurred. The smallest mass is found over *Lc* owing to the effect of the cyclonic warm sector. In the layer 4-8 km. the greatest mass occurs over *Hf*, while the least is found over *Hr* and *Lc*, with a secondary maximum over *Lf*. In the layers 8-12 km. and above 12 km. the greatest mass is found over *Hr* and the least over *Lr*. This is nearly opposite to the distribution of mass in the lower layers, thus showing the opposite effects of advection in the troposphere and in the stratosphere.

Potential Temperatures

The next element that was considered is the potential temperature. The potential temperatures were calculated from Poisson's adiabatic equation,

$$\frac{T}{\theta} = \left(\frac{P}{1000} \right)^{.288}$$

where *T* is the temperature at a pressure *P* (in millibars), and *θ* is the potential temperature. Lines of equal potential temperature are shown in Fig. 6. The dotted line represents the tropopause. At any particular level in the tropopause the minimum potential temperature is found in the rear of a surface low, while the maximum occurs in the rear of a surface high. A secondary maximum is found in the centre of a low, in the lower levels; this might be due to the condensation of water vapour in the ascending currents in the low pressure area (7). Since the axes of highs and lows lean backwards, it can be said, in general, that the potential temperature is higher over regions of high pressure than over regions of low pressure. Between 8 and 10 km. the equipotential temperature lines are nearly horizontal. In the stratosphere the variation of the potential temperatures is reversed. The higher potential temperatures are in the rear of surface lows and the lower potential

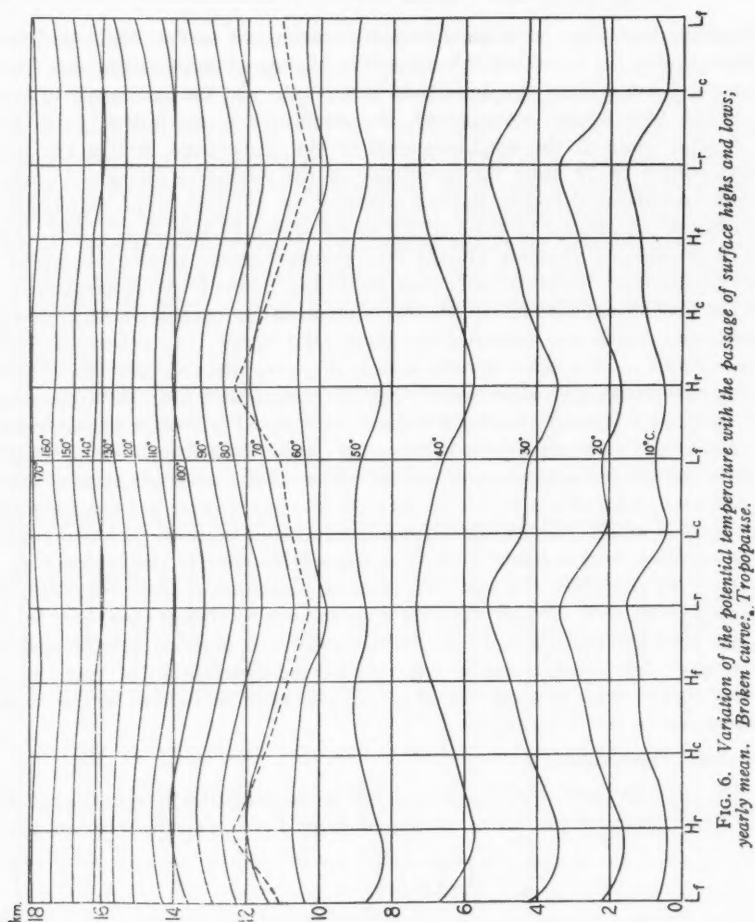


FIG. 6. Variation of the potential temperature with the passage of surface highs and lows; yearly mean. Broken curve, Tropopause.

temperatures are in the rear of surface highs. The amplitude of the variation decreases rapidly with height.

Palmén (7) arrived at a similar distribution of equipotential temperature lines in an investigation of cyclones and anticyclones. By choosing all his aerological observations in polar air masses and by arranging them so that each group contained ascents where the wind direction was from the N and from the S, he attempted to eliminate advection and to consider only vertical motions. He concluded that descending currents occur in the stratosphere where ascending currents are found in the troposphere. This would account for the fact that the minimum potential temperature in the troposphere is located over the same place as the maximum potential temperature in the stratosphere. However, this distribution of the potential temperature can

also be explained by horizontal advection in the same manner as the distribution of the temperatures. The method of attack used in this investigation stresses the effects of advection by dividing the ascents into six areas of highs and lows. Thus, only ascents with advection from approximately the same directions are grouped together. The effects of advection are not separated from those of vertical motion. Nevertheless, the same results for the distribution of equipotential temperatures are obtained as in Palmén's investigation. It seems plausible then to attribute this observed distribution of potential temperature to advection, at least in part, even though vertical motions may also be a contributing factor. Moreover, it seems doubtful that Palmén eliminated advection effects completely by his method of selecting the material. In particular it appears unlikely that advection effects in the stratosphere would also be eliminated in view of the large changes of the wind and temperature observed in passing from lower to higher layers. It may therefore be assumed that Palmén's results indicate not only the effects of vertical motion but also of horizontal advection.

Seasonal Means

To study seasonal differences that might show themselves in the distribution of pressure and temperature variations, the data were grouped according to two seasons, summer (June, July, August), and winter (December, January, February). The results are plotted in Figs. 7 to 10 and the components of the harmonic series are shown in Tables IV and V. Comparing the first

TABLE IV
HARMONIC COMPONENTS OF THE PRESSURES AND TEMPERATURES DURING THE PASSAGE
OF SURFACE HIGHS AND LOWS—SUMMER

—	A_1 , mb.	α_1 , °	A_2 , mb.	α_2 , °
P_0	5.2	250	0.2	344
P_2	4.5	257	0.8	304
P_4	3.5	277	0.9	316
P_6	3.4	288	1.1	358
P_8	3.1	297	0.9	321
P_{10}	3.3	312	1.5	335
P_{12}	2.1	309	1.1	329
P_{14}	1.1	303	1.0	286
P_{16}	1.4	301	0.8	46
P_{18}	0.6	263	0.1	270
H	0.63 km.	324	0.35 km.	342
T_0	2.1° C.	35	0.9° C.	352
T_2	1.9	350	0.9	297
T_4	1.3	335	0.4	300
T_6	1.7	321	0.7	2
T_8	2.0	332	0.6	300
T_{10}	1.3	348	0.9	339
T_{12}	1.6	122	1.3	333
T_{14}	1.9	126	0.1	210
T_{16}	1.3	150	0.7	125
T_{18}	0.9	88	1.0	148
T_H	2.7	133	0.7	7

TABLE V

HARMONIC COMPONENTS OF THE PRESSURE AND TEMPERATURES DURING THE PASSAGE
OF SURFACE HIGHS AND LOWS—WINTER

—	A_1 , mb.	α_1 , °	A_2 , mb.	α_2 , °
P_0	9.7	243	1.3	295
P_2	6.6	273	0.8	253
P_4	6.3	292	1.5	208
P_6	6.8	297	1.8	190
P_8	6.7	304	1.8	192
P_{10}	4.7	315	2.2	194
P_{12}	3.8	333	0.9	203
P_{14}	1.6	319	1.4	185
P_{16}	1.0	331	1.1	160
H	0.91 km.	300	0.28 km.	206
T_0	5.4° C.	32	1.4° C.	187
T_2	4.1	340	1.9	155
T_4	4.5	329	1.6	178
T_6	3.0	328	1.4	209
T_8	1.4	320	1.8	216
T_{10}	2.9	98	1.6	246
T_{12}	4.1	116	0.3	155
T_{14}	3.2	95	0.3	60
T_{16}	2.2	67	0.9	112
T_H	4.4	95	1.2	333

harmonic components of the pressure variation (Table IV—summer, and Table V—winter), we see that the amplitude of the pressure variation is about twice as large in winter as in summer. In summer the amplitude decreases rapidly in the first 4 km. but it remains fairly constant in the upper troposphere. In winter the amplitude decreases very rapidly in the first 2 km. so that above 2 km. the amplitude is even somewhat less than for the yearly mean values but still larger than the summer amplitudes for the corresponding heights. The phase retardation of the pressure extremes is larger in winter than in summer. This is to be expected because the temperature variation is much greater in winter than in summer. As a result, the difference in the decrease of pressure with height over H_c and H_r will be greater in winter than in summer, that is, the decrease in pressure with height over H_c is much more rapid relative to the decrease over H_r in winter than in summer because the temperature difference between H_c and H_r is so much greater in winter, H_r being the warmer. It follows that the maximum pressure will occur over H_r at a lower level in winter than in summer, in other words the retardation of the pressure extremes is greater in winter.

The phase advance of the temperature extremes is somewhat larger in winter than in summer; this presumably might be due to the higher wind velocities in the troposphere in winter. The temperature variation changes phase above 8 km. in winter and at 12 km. in summer, indicating the higher position of the tropopause in summer. In both summer and winter the amplitude of the temperature variation increases as soon as the phase reverses, i.e., there is a strong secondary maximum of temperature variation in the

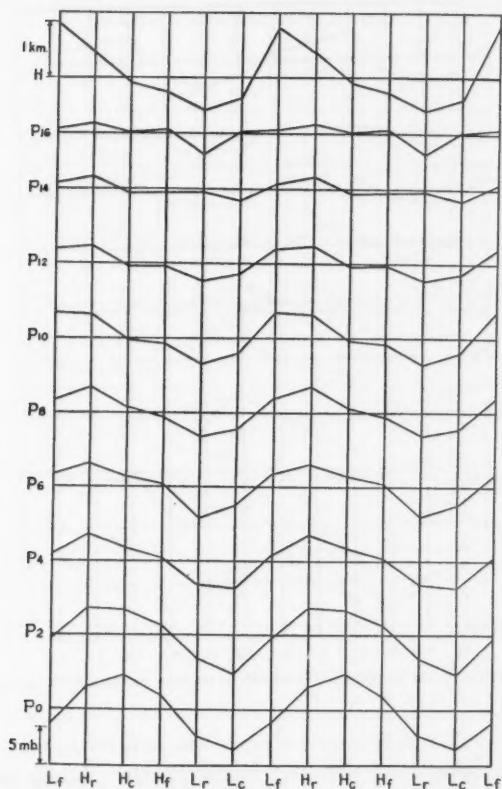


FIG. 7. Variation of the pressure and of the height of the tropopause with the passage of surface highs and lows; summer mean.

lower stratosphere in the neighbourhood of the tropopause (8 to 11 km. in winter and 12 to 13.5 in summer). Thus, the layers in the lower stratosphere are at least as effective in causing surface pressure variations as the layers in the upper troposphere, although the increase in temperature variation above the tropopause is partly offset by the decrease in the density of air with altitude. This is also in agreement with the fact that the greatest advective changes of mass occur near the surface and near the tropopause (6). The increase in the amplitude of the temperature variation, however, need not necessarily be an advective phenomenon, but could be due, at least, in part, to large vertical motions near the tropopause.

Special Case. Jan. 8-14, 1939

An attempt has been made to amplify the preceding statistical results by the presentation of individual synoptic situations. To do this, aerological observations are needed in the six areas of highs and lows. Since aerological

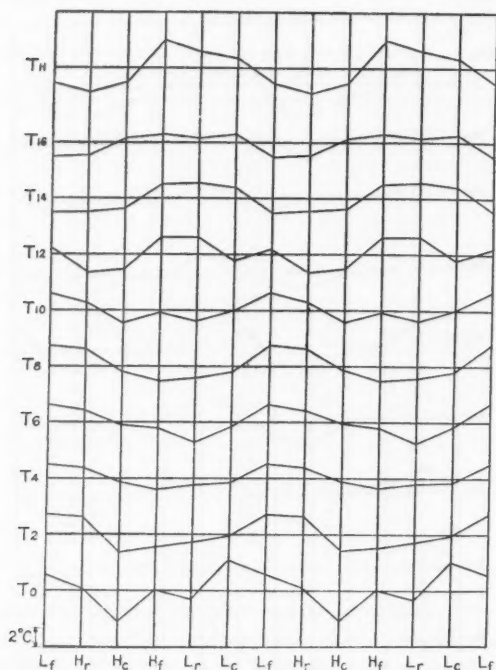


FIG. 8. Variation of the temperature with the passage of surface highs and lows; summer mean.

observations are taken only once a day, it was difficult to find a situation in which sufficient aerological material was available. Many cases failed to yield any satisfactory results, owing mainly to the fact that a time scale unit of one day is too large to reveal these effects. J. Bjerknes and E. Palmén (2) have constructed barograms at the different levels for European stations for which enough aerial ascents were available in a selected cyclone. These barograms show the retardation of the pressure extremes. In the barogram for Sealand (Fig. 21 in the reference), for example, the lowest pressure occurred between 16 and 17 h. (Feb. 16, 1935), while from 4 to 8 km. the lowest pressure is found from 19 to 20 h. Taking three to six days as a reasonable time interval from one passage to the next of a certain region (which represents 360° in the above harmonic analysis), the retardation between 0 and 8 km. (37°) for the yearly mean would be 8 to 15 hr. For the special case of Bjerknes and Palmén, the retardation between the surface and 8 km. is only about four hours, much less than the yearly mean value of 8 to 15 hr. However the above value of four hours holds for an individual European cyclone that may have had characteristics different from those of the cyclones generally found over North America. Also, polar front theory indicates that the

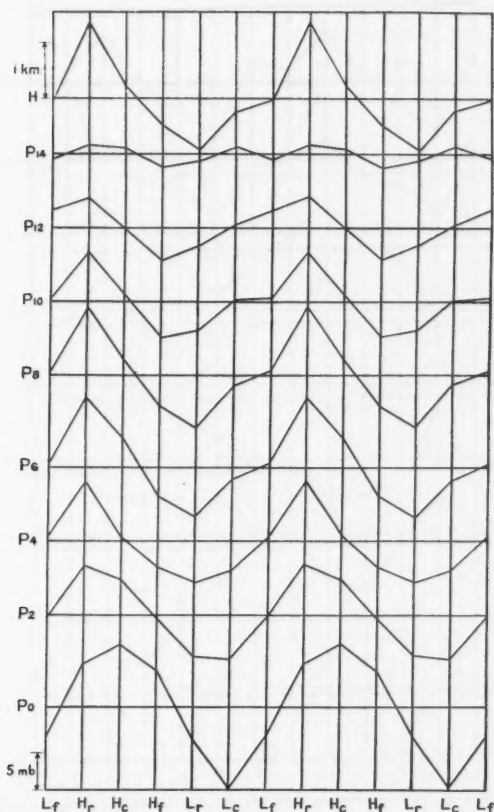


FIG. 9. Variation of the pressure and of the height of the tropopause with the passage of surface highs and lows; winter mean.

lag should be greater for younger cyclones than for older ones. Either of the above factors may contribute to the explanation of the greater time lag of the yearly mean values than of this special case.

One of the cases in this investigation for which sufficient data was available is described below.

On Jan. 8, 1939, a low, which subsequently moved NE, was developing in the southwestern United States. On Jan. 9 it was centred N of Omaha while Sault Ste. Marie was situated in the area between *Hr* of the preceding high and *Lf* of this low. On Jan. 10, Sault Ste. Marie was in the centre of the low. On Jan. 11 this slow moving low had passed over the station, leaving it in *Lr*. On Jan. 12 to 14 a polar Canadian anticyclone following the cold front associated with the low passed over Sault Ste. Marie. In Figs. 11 and

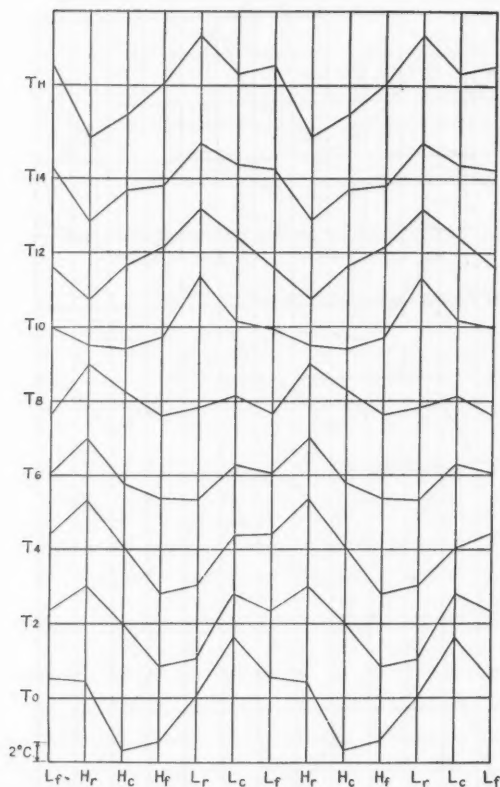


FIG. 10. Variation of the temperature with the passage of surface highs and lows; winter mean.

12 are plotted the pressures and temperatures by days. According to the diagrams the lowest pressure occurred on Jan. 10 at the surface and on Jan. 11 at higher levels. The highest temperature was observed on the 10th at the surface and on the 9th at higher levels, thus showing the retardation of the pressure extremes and the forward displacement of the temperature extremes for the low. Above the tropopause the temperature changes phase. The preceding high also shows the retardation of the pressure extremes, since the pressure at the surface was higher on Jan. 8 than on Jan. 9, while at 2 km. and above, the highest pressure was found on the Jan. 9. The high that followed the low, however, does not show the retardation of the pressure extremes.

An attempt was also made to use the aerological material from different stations to obtain a cross-section through a low. The distance between the

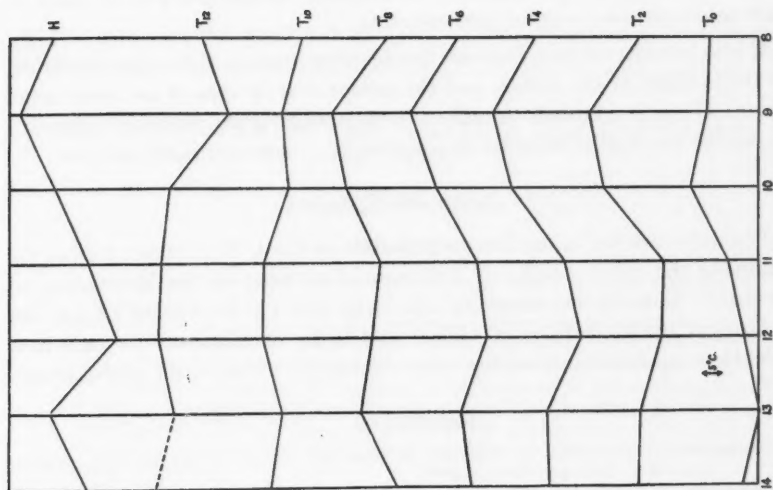


FIG. 11. Pressure variation from Jan. 8-14, 1939.

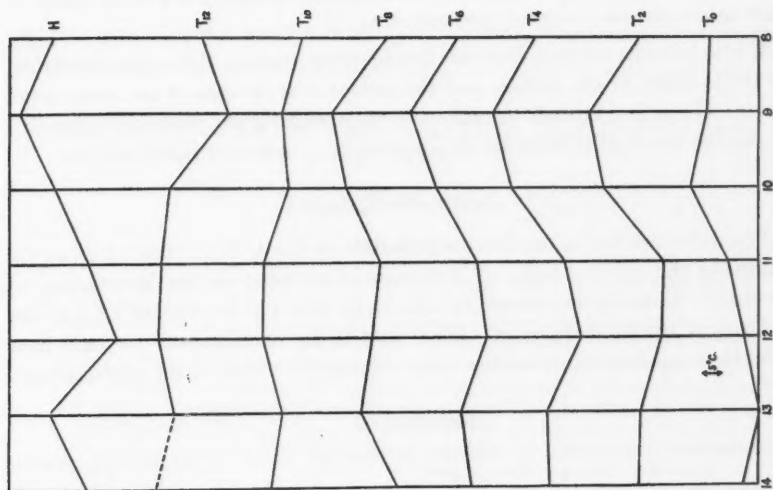


FIG. 12. Temperature variation from Jan. 8-14, 1939.

stations at present available is too large to show the displacement of pressure and temperature extremes aloft, although considerable use can be made of such cross-sections for other purposes (11).

It is to be expected that there are considerable regional differences depending on the latitude of the station and the predominating type of air mass found there. The writer intends to make a further study of the problem by investigating the aerological material at a station in a more southerly latitude.

Acknowledgments

The writer wishes to express his gratitude to the U.S. Weather Bureau for supplying the data; to Mr. J. Patterson, Controller of the Meteorological Service of Canada, for obtaining the data and for permission to use the facilities of the Meteorological Office; and to Dr. B. Haurwitz for numerous valuable suggestions and helpful advice during the course of the investigation.

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NUMBER 1

THE MECHANISM OF THE ALKALINE DELIGNIFICATION OF WOOD¹

BY G. L. LAROCQUE² AND O. MAASS³

Abstract

Measurement was made of the rate of delignification of sprucewood with lithium, barium, sodium, potassium, and tetra-ethyl ammonium hydroxides under closely controlled conditions of temperature and concentration. The reaction rates were compared with the ionic mobilities and adsorption coefficients of the different alkalis. Methanol, ethanol, and glycerol were used as solvents.

From these results a mechanism is suggested, according to which adsorption of alkali at the reaction interface is the determining factor in setting the rate of delignification. The rate is also dependent on the specific nature of the alkali cation and varies with the temperature in accordance with the general theory of thermal activation.

Introduction

The alkaline digestion of wood for the production of paper pulp is a common industrial process that has been in use for more than 50 years. Notwithstanding the commercial importance of this process, the methods employed are largely empirical and little is known of the actual physical-chemical mechanism. The present investigation is an attempt to determine the exact nature of this cooking process, which consists essentially in the treatment of wood with an alkaline liquor and heat in a pressure resisting vessel. The cooking liquor extracts most of the lignin, pentosan, and other non-cellulosic materials, leaving the desired cellulose, the yield and purity of which depend on the conditions of the pulping.

The mechanism of the process is by no means a simple one. The wood substance is not a homogenous material, but a mixture of α -cellulose, hemicelluloses, pentosan, lignin, and small amounts of extractives; and these substances vary decidedly in their chemical behaviour toward alkali. Since, however, the lignin is the most resistant of the incrusting materials present, the rate of its solution in alkali is the governing factor in the purification of the cellulose.

There are a number of secondary factors, such as the shape and size of the chip, and the density and moisture content of the wood, that may influence the delignification process. Most of these secondary factors have now been

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investigated. Thus, Larocque and Maass (4) have shown that with spruce wood and aqueous alkali, the rate of delignification was the same irrespective of the size of the sample from a wood meal of 0.0005 mm. particle size up to a limiting chip thickness of about 10 mm.

Furthermore, the density of the wood had no influence on the delignification other than that which would be expected from the higher original lignin content of the denser wood. Also, the presence of moisture in the chips was without effect other than that of diluting the liquor, and the addition of wetting agents for facilitating the penetration rate was without significant effect.

It was the purpose of the present investigation to examine some of the remaining factors capable of affecting the rate of reaction, with a view to determining what are the qualities of an alkaline liquor that render it most suitable for delignification, and in this manner to gain a new insight into the mechanism of the alkaline delignification of wood.

The experimental sequence was the following. A study of the rate of reaction indicated that it was of the apparent monomolecular type, having a definite velocity constant for each set of experimental conditions. The effect of different experimental conditions on the velocity constant was then examined, in order to ascertain the factors that really controlled the reaction rate. The variables investigated were as follows:—

The ionic properties of the alkali cation, the concentration of the hydroxyl ion, the solubility of the alkali in the solvent used, the absorption of the alkali at the reaction interface, and the influence of the temperature on the rate of reaction. From a consideration of these factors, a tentative theory has been submitted concerning the mechanism of the delignification reaction.

Experimental Procedure and Results

The experimental method used was that previously described in detail by Lusby and Maass (6). Essentially it consists in digesting for a definite time interval 10 gm. of spruce wood chips in a steel pressure-resisting cell of 80 cc. capacity. The sample having been saturated with cold liquor, the cell was immersed in a thermostatically controlled oil bath preheated to the desired temperature. A stream of caustic liquor of the desired concentration was sent through the cell at a steady rate during the digestion period, with the double object of removing the waste products of the reaction and maintaining constant the alkali concentration.

The reaction was stopped when desired by quenching the cell in water. The pulp was then removed and dried at 105° C. to determine the yield. The amount of unchanged lignin remaining in the pulp was determined by the method of Ross and Potter (12). The yield of carbohydrate was obtained by subtracting the value obtained from the yield of pulp, all yields being expressed as a percentage of the original oven dried wood. In some of the experiments, a constant flow was not considered to be necessary and a 200 cc. capacity closed bomb, containing 10 gm. of chips was used instead.

Unless otherwise indicated, the standard procedure was to employ 2.0 *N* aqueous alkali, and to allow it to digest for three hours at 160° C.

I. The Time-rate of Delignification

The first step towards a better understanding of the mechanism of the soda-delignification process was to determine the manner in which the reaction rate varied with time. It was then possible to calculate whether the reaction was proceeding in accordance with an apparent monomolecular, bimolecular, or other regular law governing chemical action.

Cooking experiments were performed in which wood samples of three different densities were cooked under identical experimental conditions for periods up to 6½ hr. Details are given in Table I.

TABLE I
THE TIME-RATE OF DELIGNIFICATION

Runs 46, 53. Bombs: Cast-iron, 200 cc. capacity, no liquor circulation. Wood: black spruce, 20 by 10 by 2 mm. chips, 10 gm. per bomb—wood density and lignin content as indicated. Liquor: aqueous sodium hydroxide, 2.0 *M*, 165 cc. per bomb.
Temp.: 160 C.

Time, hr.	Density = 0.45		Density = 0.35		Density = 0.406	
	Lignin res.	Carbohydrate yield	Lignin res.	Carbohydrate yield	Lignin res.	Carbohydrate yield
0.00	32.0	68.0	30.3	69.7	—	—
0.75	19.2	49.6	17.25	49.5	—	—
1.33	11.4	47.3	10.68	47.0	—	—
2.25	6.0	43.3	5.62	43.6	—	—
3.33	2.67	41.1	2.67	40.7	—	—
4.50	2.02	40.2	1.73	38.8	1.80	41.9
6.75	—	—	—	—	1.18	38.5

The lignin percentage remaining in the pulp as given in Table I, is shown plotted on a logarithmic scale against time in Fig. 1. A linear relation is seen to hold during the solution of all but the last 2% or so of lignin. This was first noticed by Svante Arrhenius (1), and indicates that for the most part the delignification reaction is a first order or apparent monomolecular reaction, that is, *the amount of lignin going into solution at any time is proportional to the amount of undissolved lignin still remaining in the wood at that time.*

The behaviour is that given by the relation:

$$-dL/dt = k(L_0 - L), \quad (1)$$

which can also be written:

$$k = 1/t \log_e L_0/L, \quad (2)$$

where L_0 is the original lignin content of the wood, L is the lignin remaining after a time t hours. k is the velocity constant, and is a measure of the velocity with which the reaction is proceeding for any one set of experimental conditions.

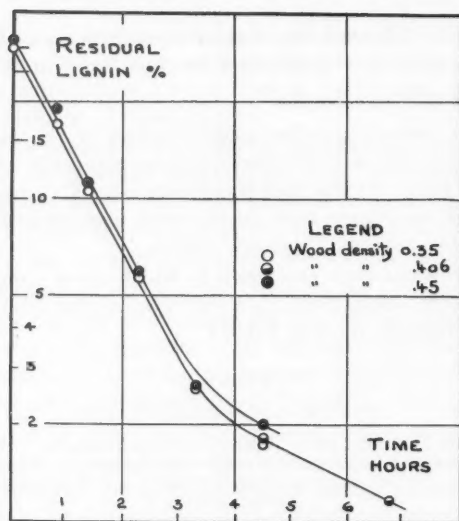


FIG. 1. Rate of delignification—2.0 M sodium hydroxide, 160° C.

The last 2% or so of lignin does not follow the monomolecular law, but dissolves at about one-quarter the rate of the bulk of the lignin. The difficulty of accurately measuring these small lignin values is not a sufficient explanation for this behaviour, since Corey and Maass (2) have shown that in the case of sulphite cooking the monomolecular relation still holds good for these low lignin values.

This behaviour has been noticed before, and the explanation offered by Mitchell and Yorston (7) is that this part of the lignin is held in the interior of the cell wall and that its outward diffusion is hindered by its relatively large particle size. It follows that velocity constants should be used only for comparing rates of delignification when these have been determined for residual lignin values greater than 2% or so.

The parallelism of the two curves also indicates that the lignin in the wood of higher density dissolves at the same rate as the lignin in the more porous wood. This confirms a previous observation by Larocque and Maass (4) that notwithstanding the greater resistance of dense wood to diffusion, wood density has no influence on delignification other than that which would be expected from the higher original lignin content of denser wood.

The conclusion to be drawn is that all the lignin in the wood seems to be equally accessible to the cooking liquor. Either the cooking liquor completely permeates the lignin substance, or more probably the area of the reaction interface between the liquor and the solid phase at any one time is proportional to the amount of lignin present in the wood.

II. The Nature of the Alkali

The second step towards the elucidation of the mechanism of soda-pulping was to determine the influence of alkalis other than sodium hydroxide, on the reaction rate, in order to find out what relation existed between the rate of delignification and the ionic properties: degree of ionization, ionic mobility, degree of hydration, coefficients of diffusion, etc., of the particular alkali used. From the manner in which the rate of delignification varied with the properties of the alkali employed, it should then be possible to put forth a theory describing the mechanism of the reaction.

Pulping was therefore carried out using the strong inorganic bases lithium, barium, sodium, and potassium hydroxides, and the strong organic base tetraethyl ammonium hydroxide. The procedure followed and the results obtained are given in Tables II and III.

TABLE II
DELIGNIFICATION BY STRONG INORGANIC BASES

Run No. 45. Bombs: Cast-iron, 200 cc. capacity, no liquor circulation. Wood: black spruce, density 0.406, 20 by 10 by 2 mm. chips, 10 gm. per bomb. Liquor: Aqueous lithium, barium, sodium, and potassium hydroxides—165 cc. per bomb. Temp.: from 100 to 160° C. for one hour, then at 160° for three hours.

	LiOH	Ba(OH) ₂ *	NaOH	KOH
Carbohydrate yield, %	45.5	27.4	41.3	41.6
Lignin yield, %	6.6	3.8	2.5	1.83
Velocity constant	0.51	0.69	0.83	0.94

* With the barium hydroxide liquor, the barium alkali-lignin compound formed during the reaction is insoluble in the cooking liquor and remained adhering to the pulp. Consequently, this pulp was extracted with 5% hydrochloric acid to free it from barium, then with 1% sodium hydroxide to dissolve the changed lignin. The small residue of uncooked lignin remaining in the pulp was then determined in the usual manner.

TABLE III
DELIGNIFICATION BY A STRONG ORGANIC BASE

Run 69. Same procedure as in Run 45 except that only 150 cc. of 0.70 M tetra-ethyl ammonium hydroxide was used per bomb. Sodium hydroxide was also used for purposes of comparison.

	NaOH	(C ₂ H ₅) ₄ NOH
Carbohydrate yield, %	46.5	46.0
Lignin yield, %	14.8	5.52
Velocity constant	0.241	0.57

The values obtained for the velocity constants rank the alkalis in the following order of increasing reactivity: lithium hydroxide, barium hydroxide, sodium hydroxide, potassium hydroxide tetra-ethylammonium hydroxide. The observed differences in reaction rate must necessarily have depended on some differences in the properties of the alkaline ions involved, and may have been due to:

- (1) Differences in their degree of dissociation,
- (2) Differences in ionic mobility caused by hydration of the ions,
- (3) Differences in the degree to which they are absorbed by the lignin, on the assumption that absorption of alkali is a necessary prerequisite to reaction,
- (4) Variation in the chemical affinity which the lignin substance has for the different alkalis.

These four possibilities are considered separately:

The degree of dissociation of these alkalis at 160° C. is not on record. Conductivity and viscosity data do exist, however, which makes it possible to calculate the dissociation of lithium hydroxide, sodium hydroxide, and potassium hydroxide relative to one another with a fair degree of accuracy. The values obtained were 1.00, 1.11, and 1.19 respectively for each of these alkalis, and are too much alike to account for the marked differences in their rates of delignification.

The presence of a sufficient hydroxyl ion concentration, corresponding to a pH value of 12 or 13, is necessary in the alkaline delignification of wood, but the above considerations indicate that the reaction rate is also dependent on some special property of the cation employed, other than its degree of dissociation.

Differences in the mobility of the cations might account for the different rates of delignification. In Table IV are given the relative velocity constants and ionic mobilities of the four strong inorganic alkalis, based on unity for lithium hydroxide.

TABLE IV
IONIC MOBILITIES AND VELOCITY CONSTANTS

Alkali	LiOH	Ba(OH) ₂	NaOH	KOH
Velocity constant	1.00	1.35	1.62	1.84
Ionic mobility	1.00	1.67	1.31	1.94

Although there is a rough analogy between the ionic mobility and the velocity of delignification, diffusion cannot be the main factor governing the reaction velocity since it has been shown (13) that the temperature coefficient of diffusion of aqueous sodium and potassium hydroxide solutions is 1.2 for a 10° rise in temperature, whereas the observed temperature coefficient is materially greater, namely, from 1.7 to 2.7 at 160°, the exact value depending upon the particular concentration and the alkali used. In such a case where

the observed temperature coefficient of the reaction velocity is greater than the coefficient of diffusion, it follows (11) that the observed reaction velocity is the true chemical velocity constant k independent of viscosity considerations.

TABLE V
YIELDS OF CARBOHYDRATE AND LIGNIN IN THE ALKALINE DELIGNIFICATION OF SPRUCEWOOD

Concentration, <i>M</i>	Time, hr.	Carbohydrate, %	Lignin, %
<i>Lithium hydroxide</i>			
1.38	1.0	42.2	17.2
*2.0	3.0	44.5	6.9
2.89	1.0	47.3	15.4
*4.5	1.0	46.0	13.0
<i>Sodium hydroxide</i>			
1.4	0.5	44.8	32.6
	1.0	42.4	32.1
	1.5	42.0	23.5
	2.0	41.5	20.3
	3.0	39.0	15.3
2.0	3.0	42.0	3.6
2.9	0.5	44.7	30.6
	1.0	41.0	22.1
	1.5	40.7	15.6
	2.0	37.5	9.7
	3.0	32.7	7.0
4.5	0.5	49.7	29.6
	1.0	42.0	17.9
	1.25	39.4	13.8
	2.0	33.0	5.1
	3.0	28.2	4.3
6.2	1.0	38.5	6.4
8.1	1.0	39.1	5.4
	3.0	27.0	1.5
9.74	1.0	38.3	6.8
	3.0	28.7	0.8
<i>Potassium hydroxide</i>			
1.4	1.0	45.3	15.0
*2.0	3.0	39.1	0.9
2.9	1.0	42.6	19.5
	1.5	41.9	15.0
4.56	0.5	48.4	22.4
	1.0	39.9	15.3
6.26	1.0	44.0	3.4
9.6	1.0	45.0	1.6
14.2	1.0	41.5	0.6

III. The Effect of Concentration

The next step was to investigate how the velocity constant varied with the concentration. Three alkalis, namely: lithium, sodium and potassium hydroxides were used at concentrations of from 1.4 to 14 *M*. The experiments were carried out at 160° C. according to the previously described standard procedure. The results obtained are reported in Table V. Those values preceded by an asterisk have been experimentally determined in the present investigation. The remainder of the data has been calculated from the results of Lusby and Maass (6).

The residual lignin values follow the monomolecular law in that they tend to fall on a straight line when plotted logarithmically.

From the slopes of these curves mean values have been calculated for the velocity constant at every concentration. The values are reported in Table VI.

TABLE VI
VELOCITY CONSTANTS AND CONCENTRATION OF ALKALI IN THE DELIGNIFICATION OF WOOD

Molarity	<i>k</i>	Molarity	<i>k</i>
<i>Lithium hydroxide</i>			
1.38	0.53	2.89	0.66
1.97	.59	4.5	.80
<i>Sodium hydroxide</i>			
1.4	0.65	6.2	1.55
2.0	.84	8.1	1.71
2.9	1.06	14.2	2.77
4.5	1.40		
<i>Potassium hydroxide</i>			
1.4	0.71	6.2	2.19
2.0	1.16	9.6	2.95
2.9	1.28	14.2	3.92
4.5	1.89		

The velocity constants for the three alkalis calculated in this manner have been plotted on a concentration basis in Fig. 2. The curves obtained indicate the manner in which the reaction velocity increases with the concentration for each of these alkalis.

The resemblance of these curves to Freundlich's absorption isotherms suggests that the rate of reaction might depend on the absorption of alkali at the liquor-lignin interface. This would be a necessary prerequisite to chemical action and for any one alkali the rate of reaction would depend on the concentration of the absorbed alkali. Further evidence is available from direct measurements of absorption and from pulping experiments in alcoholic solutions.

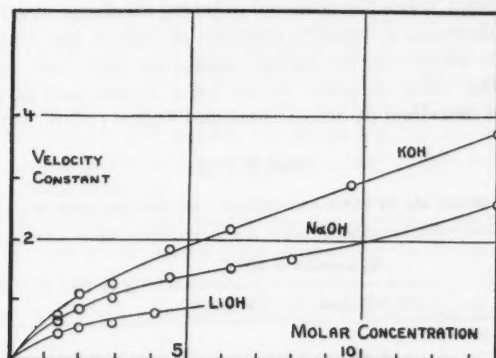


FIG. 2. Reaction velocity and concentration.

IV. The Absorption of Alkali

Lusby and Maass (5) have shown that the sorption of alkali on spruce wood at any concentration is proportional to the sorption on cotton at that concentration. The cotton sorption values of Dehnert and König (3) can, therefore, be legitimately compared to the velocity constants obtained previously, as shown in Table VII.

TABLE VII

THE SORPTION OF ALKALI BY COTTON AND THE VELOCITY OF DELIGNIFICATION OF SPRUCEWOOD

Molarity	Sorption at 20° C.	k at 160° C.	Adsorption/k
<i>Sodium hydroxide</i>			
1.4	0.30	0.648	0.442
2.0	.38	.845	.450
2.9	.45	1.06	.424
4.5	.52	1.40	.371
6.2	.52	1.56	.334
8.1	.88	1.71	.513
<i>Potassium hydroxide</i>			
1.4	0.26	0.708	0.367
2.9	.41	1.28	.321
4.5	.51	1.84	.277
6.2	.52	2.19	.237
9.6	.57	2.95	.193

For any one alkali the values for the velocity constant of delignification are seen to be only roughly proportional to the cotton sorption values, as would be expected from the differences in temperature of the sorption and cooking processes, but nevertheless they suggest a certain relation between the two.

On the other hand, when the action of different alkalis on wood is considered, the observed differences in velocity constant are not in any way proportional to the extent to which the individual alkalis are absorbed, as indicated in Table VIII. The wood sorption values were determined according to the titration method described by Richardson and Maass (10, p. 3069).

TABLE VIII

THE ABSORPTION OF ALKALI BY WOOD AND COTTON, AND THE VELOCITY OF DELIGNIFICATION

Alkali	Adsorption at 20° C.		<i>k</i> at 160° C.	Absorption/ <i>k</i>
	On cellulose	On wood		
2.0 <i>M</i> LiOH	0.48		0.59	0.81
2.0 <i>M</i> NaOH	0.38		0.845	0.45
2.0 <i>M</i> KOH	0.32		1.16	0.28
0.7 <i>M</i> (C ₂ H ₅) ₂ NOH		0.70	0.57	1.23
0.7 <i>M</i> NaOH		0.63	0.24	2.62
0.7 <i>M</i> NH ₄ OH		0.30	Negligible	—

This evidence is sufficient to conclude that differences in the magnitude of sorption of different alkalis will not account for differences in their reaction rate. Experiments with different solvents will add further evidence, however, that for any one alkali, the reaction velocity is proportional to the extent of the sorption.

V. The Effect of the Solvent

Instead of using aqueous solutions, delignifications were carried out with methyl and ethyl alcohols since they are good solvents for sodium hydroxide and are in many respects similar to water. Both technical 95% alcohol and alcohol freed from water by twice distilling over lime were used. The methyl alcohol was a technical grade and over 99.5% pure. The results obtained are given in Table IX.

TABLE IX

THE EFFECT OF THE SOLVENT ON THE DELIGNIFICATION OF WOOD

Solvent	Time	Carbohydrate, %	Lignin, %
Water	3 hr.	41.3	2.5
	1½ hr.	47.0	11.5
Absolute ethyl alcohol	3 hr.	20.7	.2
Technical ethyl alcohol	3 hr.	30.6	.2
	1½ hr.	35.1	1.4
	55 min.	41.4	2.1
	30 min.	49.5	3.7
Methyl alcohol	1½ hr.	41.3	3.2

The lignin values indicate that alcoholic solutions of sodium hydroxide are considerably more effective for delignification than aqueous solutions of the same concentration. The yield of carbohydrate is also lower and it was found that a considerable fraction of the lignin originally present in the wood is completely disintegrated and cannot be accounted for in the waste liquor. This is an indication of the greater chemical activity that sodium hydroxide possesses in alcoholic solutions.

This increased rate of delignification can be explained on the basis of the partition law (9) and lends considerable support to the previously mentioned "adsorption" theory of delignification.

The solubility at 20° C. of sodium hydroxide in each of the solvents used was found to be:

<i>Solvent</i>	<i>Solubility</i>
Water	20.1 moles per litre
Methyl alcohol	5.6
Ethyl alcohol	3.57

Since each of these saturated solutions is in equilibrium with solid sodium hydroxide, the partition law applied to such a case states that the "escaping tendency" of the sodium hydroxide, that is, its tendency to leave the saturated solution and enter another phase will be the same for each of the solutions. If however, with any particular solvent the concentration is less than saturation, it follows that the escaping tendency will be given by the fractional value that the observed concentration will bear to the saturation concentration for that solvent.

The magnitude of this escaping tendency is a measure of the extent to which the dissolved substance tends to pass off as a gas, to dissolve in a second non-miscible fluid phase, or to become sorbed on a solid surface.

The escaping tendency of sodium hydroxide in 2.0 *M* aqueous or alcoholic solutions is then calculated by dividing the saturated solubility by the molarity, as indicated in Table X.

TABLE X
THE ESCAPING TENDENCY OF 2.0 *M* SODIUM
HYDROXIDE IN ALCOHOLS AND WATER

Solvent	Escaping tendency
Water	$2.0/20.1 = 0.100$
Methyl alcohol	$2.0/5.6 = 0.357$
Ethyl alcohol	$2.0/3.57 = 0.56$

A certain parallelism is found to exist between the escaping tendency and the absorption of alkali in alcoholic solutions as determined by Vieweg (14).

TABLE XI

THE RELATION OF THE VELOCITY OF DELIGNIFICATION TO THE ESCAPING TENDENCY AND THE SORPTION OF ALKALI FOR THREE SOLVENTS

Solvent	Escaping tendency	Sorption	k	Escaping tendency/ k
Water	0.100	1.00	0.84	0.12
Methyl alcohol	0.357	8.8	1.79	0.19
Ethyl alcohol	0.560	9.8	3.74	0.15

The explanation offered for this increased delignification is that owing to the greater escaping tendency of sodium hydroxide in these solvents, the sodium hydroxide has an increased affinity for the solid phase, which results in a greater absorption of alkali at the reaction interface and in a correspondingly greater reaction velocity.

This increased reaction velocity cannot be ascribed to an increase in the degree of dissociation of the sodium hydroxide since it is known that it is the reverse phenomenon that takes place. Nor can it be due to differences in viscosity since the viscosities of water, methyl alcohol, and ethyl alcohol at 30° C. are respectively 0.008, 0.005, and 0.01 in C.G.S. units.

It was interesting to determine whether a solvent of high viscosity would retard the rate of delignification of wood. Glycerol was selected since it is an alcohol and is similar in some respects to water, and to ethyl and methyl alcohols. It is a fairly good solvent for sodium hydroxide and has a viscosity 600 times that of water and 500 times that of ethyl alcohol.

In Table XII are given the yields of lignin and carbohydrate of two cooks made under comparable conditions with water and glycerol as solvents.

TABLE XII

GLYCEROL AS A SOLVENT

Solvent	Carbohydrate, %	Lignin, %
Water	47.0	11.5
Glycerol	53.4	14.9

The solubility of sodium hydroxide is less in glycerol than in water, so that the different escaping tendency of 2.0 *M* sodium hydroxide in glycerol cannot be considered as a reason for the lesser delignification observed.

It is probable that, in this case, the high viscosity of the solvent hinders the submicroscopic diffusion of the alkali into the lignin gel-structure, resulting in a lower rate of diffusion than would otherwise occur. Thus, under extreme conditions, viscosity of the medium can be a factor influencing the reaction rate.

A cooking experiment was carried out using 2.0 *M* sodium ethylate dissolved in absolute alcohol, in order to ascertain whether delignification would take place in the absence of hydroxyl ions.

Only a slight amount of pulping took part in the outside of the chips. The interior was hard, light in colour, and completely uncooked.

Sodium ethylate, $\text{Na}^+\text{OC}_2\text{H}_5^-$, is therefore not a pulping agent. The slight amount of pulping that did take place was very likely due to the action of sodium hydroxide, formed in small amount from the sodium ethylate by traces of moisture still present in the wood or in the liquor.

The presence of a sufficient hydroxyl ion concentration, in addition to a suitable alkali cation is therefore necessary for the delignification process.

VI. The Influence of Temperature on the Reaction Rate

No experimental work on the influence of temperature was performed in the present research. However, the object of the investigation, namely, the elucidation of the mechanism of alkaline pulping, required that the temperature data of other investigations should be examined and reinterpreted in the light of the Arrhenius equation and the general theory of chemical activation (8).

Arrhenius observed that the variation with temperature of the velocity constant for a number of chemical reactions could be represented by an equation of the type:

$$\ln k = B - A/T,$$

in which *A* and *B* are specific constants for each reaction. Recognizing the similarity of this equation with the van't Hoff isochore, which connects the equilibrium constant, *K*, of a chemical reaction with the increase in internal energy, *U*,

$$\ln K = \text{const} - U/RT,$$

he suggested by analogy the existence of an equilibrium between "passive" molecules of the reacting species and "active" molecules formed from normal molecules by absorption of energy.

Of the total number of molecules, only that small fraction that is "active" at any instant during the reaction can react. The result is that the chemical reaction is not instantaneous, but occurs at a measurable rate, since the special distribution of energy that is required takes a finite time. The general correctness of this view has received overwhelming confirmation.

Putting $B = \ln Z$ and $A = E/R$, the above relation can be written:

$$\ln k = \ln Z - E/RT$$

or,

$$k = Ze^{-E/RT},$$

where *Z* and *E* are the new specific constants, and *R* is the gas constant.

The fraction $e^{-E/RT}$, according to the Maxwell-Boltzmann distribution law, is proportional to the number of molecules possessing an energy content *E*. *E* is termed the critical energy and is determined experimentally by plotting the logarithm of the velocity constant against the reciprocal of the absolute

temperature. The slope of the line multiplied by the gas constant R (1.985 cal. per degree) gives the value of E in calories per gram-mole.

Applying this theory to some results obtained by Lusby, and calculating the values of k from the relation: $k = 1/t \ln L_0/L$, we obtain the data in Table XIII.

TABLE XIII
THE INFLUENCE OF TEMPERATURE ON THE REACTION VELOCITY

Temp., °C.	2.9 M NaOH		14.3 M NaOH		14.3 M KOH	
	L_r	k	L_r	k	L_r	k
120	—	—	24.1	0.184	23.6	0.205
140	23.2	0.223	11.7	0.91	4.6	1.84
160	10.4	1.026	1.9	5.03	0.6	6.18

These results are shown plotted in Fig. 3 and indicate that, taking into consideration the accuracy with which k can be determined, the straight line relation between $\ln k$ and $1/T$ is closely obeyed. We may then conclude that:

(i) In alkali-pulping, with sodium or potassium hydroxide, at both high and low alkali concentrations, this increase in the rate of delignification with increase in temperature takes place in the manner predicted by the activation theory of Arrhenius.

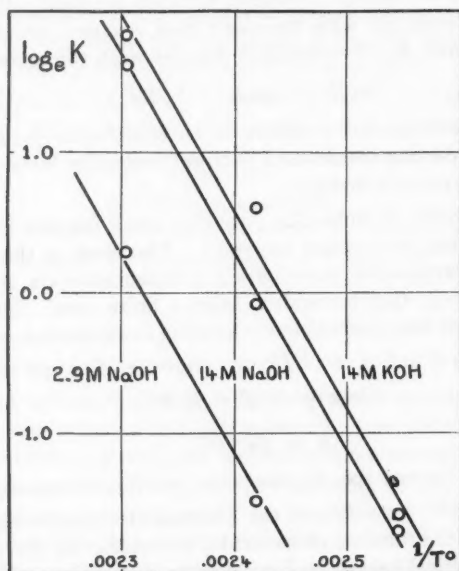


FIG. 3. Temperature coefficient of delignification.

(ii) The value of the energy of activation is found to be 32,000 cal. per gram-molecule, or 5.3×10^{-20} cal. per molecule.

(iii) The same activation energy is obtained whether 2.9 *M* sodium hydroxide, 14.3 molar sodium hydroxide, or 14.3 molar potassium hydroxide is used.

(iv) The calculated values for *Z* are:

$$\begin{aligned} 2.9 \text{ } M \text{ NaOH} &: 1.5 \times 10^{16} \text{ per hr.} \\ 14.3 \text{ } M \text{ NaOH} &: 7.0 \times 10^{16} \text{ per hr.} \\ 14.3 \text{ } M \text{ KOH} &: 8.8 \times 10^{16} \text{ per hr.} \end{aligned}$$

Conclusion

The writers have given some evidence suggesting that absorption of alkali at the reaction interface was the determining factor in setting the rate of delignification. Let us consider the molecular phenomena that are taking place at a point on the solid lignin surface.

There are three separate stages to the reaction. (i) The acidic phenolic groups in the lignin complex bring about absorption of alkali at the interface. There is no hindrance to this absorption. The interface is at all times in saturated equilibrium with the alkali in the liquid phase, since we have seen previously that the diffusion of alkali to the solid-liquid interface is always sufficiently rapid so as not to influence the reaction rate. The amount of alkali present depends on the escaping tendency of the solution. (ii) Either immediately following absorption, or after a certain interval of time, chemical combination takes place between the lignin and the absorbed alkali. (iii) There then follows a chemical hydrolysis and the separation of one alkali-lignin complex from the lignin surface, and its solution in the liquor.

We have no method of distinguishing the "combination" reaction from the "solution" reaction. We do not know whether they take place simultaneously or whether one is slower than the other and governs the reaction rate. But since the variation of the velocity of the complete reaction with temperature takes place in accordance with the Arrhenius equation, some intermediate complex must be formed between the absorbed alkali and part of the lignin, and this molecular complex requires a certain minimum energy of activation for further reaction. The energy that must be concentrated at a point of the lignin structure, in order to bring into solution one alkali-lignin complex (and incidental by-products), has been calculated to be of the order of 5.3×10^{-20} cal.

At the interface between the lignin and the absorbed alkali the complicated molecular orientations brought about by valence forces are being constantly disturbed and changed by forces of thermal agitation. By analogy with homogeneous bimolecular reactions, the constant will be the number of "favourable orientations" of the lignin-alkali complex occurring per second, any one of which, if suitably activated by an energy *E*, will result in the solution of one alkali-lignin particle.

With increase in concentration, the observed increase in the value of velocity constant k and in the value of Z , would be due to the greater number of favourable orientations rendered possible by the higher concentration of absorbed alkali at the lignin interface. Similarly, the increase in the value of k with the nature of the alkali in the order lithium hydroxide, sodium hydroxide, potassium hydroxide, would be due to the greater number of favourable orientations possible with the smaller potassium ions than with the more highly hydrated lithium and sodium ions.

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STUDIES ON ANTIOXIDANT ACTIVITY

I. ESTIMATION OF ANTIOXIDANT ACTIVITY IN STABILIZING VITAMIN A IN OILS¹

By W. E. PARKER², A.C. NEISH,³ AND W. D. MCFARLANE⁴

Abstract

The efficiency of wheat-germ oil in stabilizing vitamin A against the destructive action of ultra-violet radiations was investigated. A rapid and convenient method of estimating antioxidant potency is described which is based on ultra-violet irradiation of mixtures of halibut liver oil and antioxidant in chloroform solution and estimation of vitamin A by the direct application of the antimony trichloride reaction employing photoelectric colorimetry.

Introduction

The destruction of vitamin A in rancid oils was first noted by Fridericia (3) and Powick (14) in 1925, and confirmed by Mattill (12) two years later. Whipple (16) and Lowen, Anderson, and Harrison (11) have shown that in oils undergoing oxidation the decrease in vitamin A is paralleled by an increase in peroxide value. Extensive experiments by Lease *et al* (10) indicated that rancid fats destroyed vitamin A in the stomachs of test animals and that high peroxide values in oil supplements decreased the amount of vitamin stored in the liver. The similarity between the oxidation of fat and the destruction of vitamin A is indicated by the fact that both processes are accelerated by the presence of metallic ions, by ultra-violet light, and by increased temperature, and are retarded by antioxidants.

Various procedures for measuring the susceptibility of fats to oxidative changes and the efficiency of antioxidants have been described in the literature (9). Most of these are based on manometric measurements of the uptake of oxygen by the oil or on the time required for its content of peroxide oxygen to reach an arbitrary value. Greenbank and Holm (4) have described a photoelectric method of measuring the length of the induction period, based on the reduction of methylene blue by the oxidizing oil. Acceleration of the oxidation of the oil by heat is commonly employed to reduce the time necessary for carrying out determinations; ultra-violet light (15) and metallic catalysts (7, 15) have been used to a limited extent for the same purpose. Even under these conditions the procedures are too long to permit their general use as routine methods of analysis. No systematic investigation of the effect of antioxidants on the stability of vitamin A in oils has yet been reported, although hydroquinone (5, 6), lecithin (5), and ground cereals (11) have been shown to protect the vitamin in varying degrees.

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The comparatively rapid decomposition of vitamin A by ultra-violet radiations (2, 13) suggested to the writers the possibility of measuring the antioxidant potency of different substances by comparing the protection they afforded to vitamin A in oils exposed to ultra-violet irradiation.

Experimental

The vitamin A content of the oils was determined by the Dann and Evelyn (1) modification of the Carr-Price antimony trichloride reaction. Wilkie's (17) procedure for saponification was employed where a non-saponifiable residue was required. Peroxide oxygen was determined by the method of C. H. Lea (8).

To avoid the time-consuming saponification procedure if at all possible, a number of oils from different sources were tested to determine whether the values obtained for vitamin A on an oil directly agreed with those obtained on its non-saponifiable residue. The results, summarized in Table I, show that there is some substance present in cod liver oil that inhibits the full development of the blue colour. This fact is well known, but it will be noted that the inhibiting substance is not present in halibut liver oil or in pilchardene. Measurements of the rate of fading of the blue colour showed that there was little difference in this respect when the oil, or its non-saponifiable fraction, was used for the test. As a result of these experiments either halibut liver oil or pilchardene was used in all subsequent experiments.

For the first tests of antioxidant activity a sample of wheat-germ oil prepared by a solvent-extraction process was employed. Although this oil contained relatively large quantities of carotinoid pigments (75 micrograms per 100 gm. of oil) it was found that an equivalent amount of carotene added

TABLE I

THE EFFECT OF SAPONIFICATION ON THE VITAMIN A VALUE OF OILS
AS DETERMINED BY THE ANTIMONY TRICHLORIDE METHOD

Sample	Vitamin A, International units per gram of oil	
	With saponification	Without saponification
Cod liver oil No. 1	1180	795
No. 2	2415	1425
No. 3	546	360
Clo-trate (Cod liver oil)	2250	1950
Pilchardene No. 1	735	735
No. 2	1980	1980
No. 3	2025	2170
Halibut liver oil No. 1	54500	53100
No. 2	89250	89250

to pilchardene did not significantly affect the results of the vitamin A determinations. The values for vitamin A obtained with mixtures of pilchardene and wheat-germ oil were slightly higher than calculated, but this was due to a slight cloudiness that developed on the addition of the antimony trichloride reagent, rather than to an enhanced blue colour.

A. Direct Irradiation of Oil Mixtures

Portions (10 ml.) of mixtures of pilchardene with wheat-germ oil were irradiated simultaneously in 30 ml. beakers placed directly beneath a Hanovia

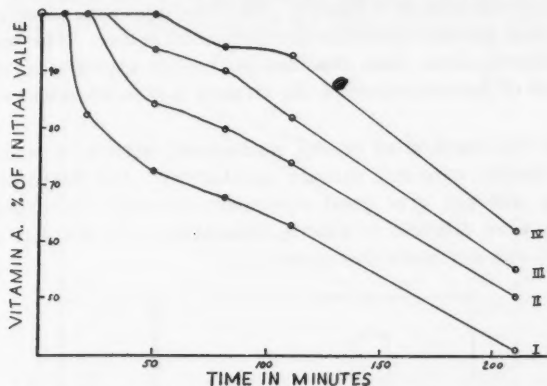


FIG. 1. The destruction of vitamin A in pilchardene and mixtures of pilchardene with wheat-germ oil by irradiation with a quartz mercury arc.

- I. 100% pilchardene.
- II. 95% pilchardene + 5% wheat-germ oil.
- III. 80% pilchardene + 20% wheat-germ oil.
- IV. 50% pilchardene + 50% wheat-germ oil.

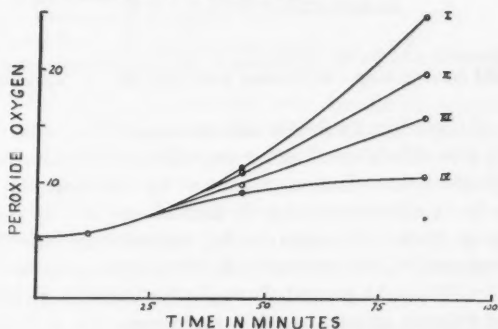


FIG. 2. The increase in peroxide oxygen in pilchardene and mixtures of pilchardene with wheat-germ oil, by irradiation with a quartz mercury lamp. The peroxide oxygen is expressed in terms of 0.002 N thiosulphate per ml. of oil.

- I. 100% pilchardene.
- II. 95% pilchardene + 5% wheat-germ oil.
- III. 80% pilchardene + 20% wheat-germ oil.
- IV. 50% pilchardene + 50% wheat-germ oil.

quartz mercury arc 17 cm. from the surface of the oil. At intervals, 1 ml. aliquots were removed, dissolved in chloroform, and their vitamin content determined. The results, shown graphically in Fig. 1, indicated a definite inhibition of the decomposition of the vitamin by the wheat-germ oil, and an increased induction period. Irradiation also increased the peroxide values of the irradiated oil mixtures (Fig. 2).

There was a possibility that the results were affected by the difference in concentration of vitamin A in the mixtures. To test this, fresh mixtures were prepared in which the concentration of vitamin was kept constant by the addition of petrolatum as a diluent. The mixtures were irradiated, and the vitamin A and peroxide contents determined as before. The results did not differ significantly from those obtained in the first experiment, and indicated that the rate of decomposition of the vitamin was independent of its concentration.

Although this method of testing antioxidant activity was comparatively rapid, the results were not entirely satisfactory. Oil mixtures of identical composition did not give good agreement in duplicate experiments, the viscous oils were difficult to pipette accurately, and the heating from the mercury arc was not controlled in any way.

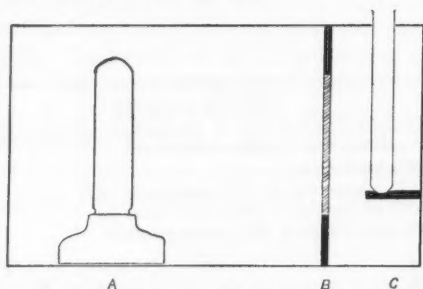


FIG. 3. Apparatus used for the irradiation of oils in chloroform solution. A. General Electric Type H3 mercury lamp. B. Corning Filter No. 986. C. Rack and test tubes.

Irradiation of the oil in a suitable solvent appeared to offer the best means of overcoming the difficulty of removing aliquots for analysis, and of the various fat solvents, chloroform appeared to be the most suitable. Vitamin A is known to be relatively unstable in this solvent (2, 13) and its use would permit antimony trichloride tests to be carried out directly without the necessity of evaporating any solvent. Preliminary experiments showed that sufficient ultra-violet light passed through the walls of Pyrex test-tubes to decompose the vitamin at a reasonably rapid rate.

B. Irradiation in Chloroform Solution

For more extensive tests the apparatus illustrated in Fig. 3 was constructed. The light source (A) was a General Electric Type H3 mercury lamp, and was placed at a distance of 8 in. from a rack (C), which held three 16 by 150 mm.

Pyrex test-tubes. A No. 986 Corning filter (B) placed between the light source and the tubes protected the latter from excessive heat and from visible light, but transmitted 90% of the ultra-violet radiation at 3300 Å. The entire apparatus was enclosed in a well ventilated box.

With this apparatus very consistent results were obtained for the rate of decomposition of vitamin A. Irradiation of a chloroform solution of halibut liver oil for one hour reduced its vitamin A content to 42% of its original value, and this result could be closely duplicated with different concentrations of the oil. The addition of wheat-germ oil reduced the rate of decomposition of the vitamin, and slightly increased the induction period (Fig. 4).

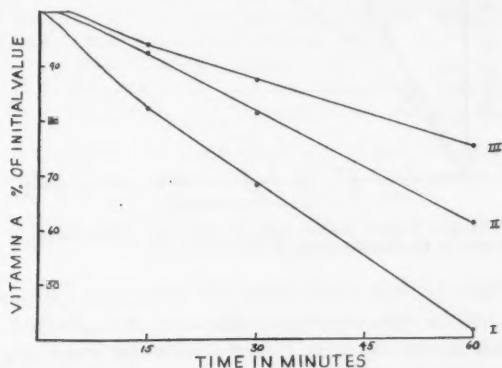


FIG. 4. The destruction of vitamin A in halibut liver oil, and mixtures of halibut liver oil with wheat-germ oil, by ultra-violet irradiation in chloroform solution.

- I. Halibut liver oil.
- II. Halibut liver oil + 4% expressed wheat-germ oil.
- III. Halibut liver oil + 4% extracted wheat-germ oil.

In carrying out tests of antioxidant activity with this apparatus, the following technique was adopted. Three tubes containing halibut liver oil in chloroform in the same concentration were irradiated simultaneously. In addition to the halibut liver oil one contained 4% of wheat-germ oil which was adopted as a standard; the second contained a known weight of the oil being tested. No addition was made to the third tube, which served as a control. At the end of 15, 30 and 60 min. intervals, 1 ml. aliquots were removed and analyzed immediately for vitamin A. Typical decomposition curves (Fig. 4) are very similar to those obtained by Holmes (5) who used heat to accelerate the decomposition of the vitamin.

In order to obtain a numerical comparison of the antioxidant efficiencies of different oils as determined by this method the writers propose to employ the term "protection factor" for the ratio defined by the following equation.

$$\text{Protection factor} = \frac{x-y}{x},$$

where x = the percentage of vitamin A destroyed by irradiation for one hour

in chloroform solution in the absence of antioxidant, and y = the percentage of vitamin A destroyed under the same conditions in the presence of an antioxidant.

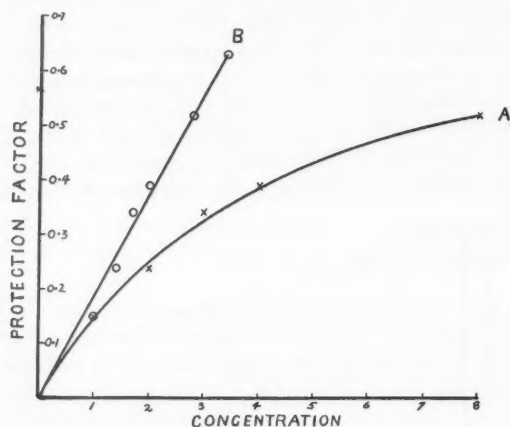


FIG. 5. Protection factors plotted against—(A) the concentration of wheat-germ oil, (B) the square root of the concentration of wheat-germ oil.

Protection factors have been calculated from the experimental results for different oils, and for different concentrations of the same oil. The protection factor does not appear to vary directly with the concentration of the oil, but the points obtained by plotting the square root of the concentration against protection factors fall approximately on a straight line passing through the origin (Fig. 5).

TABLE II

THE REPRODUCIBILITY OF RESULTS ON REPEATED IRRADIATION OF HALIBUT LIVER OIL WITH AND WITHOUT WHEAT-GERM OIL

Antioxidant	Strength, %	Number of determinations	% Vitamin A destroyed in one hour	Protection factor
None	—	18	58.5 \pm 0.5	—
Oil No. 1	2	3	35.2 \pm 0.6	0.40
Oil No. 1	4	3	27.8 \pm 0.4	0.52
Oil No 2	4	15	35.4 \pm 0.3	0.39

Table II illustrates the reproducibility of the results that have been obtained by the method. Protection factors, calculated as described above, are also included. The consistency with which the results could be duplicated with solutions of identical composition leads to the belief that it might be possible to dispense with control solutions. However, they have always been included as a precautionary measure against marked fluctuations in line voltage.

Different samples of wheat-germ oil, fractions obtained from wheat-germ oil by different methods of treatment, and pure substances reported to possess antioxidant activity have been tested by this method. The results of these investigations will be published in the second paper of this series.

Acknowledgment

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SYNTHESIS OF VERATROYL ACETALDEHYDE AND INFLUENCE OF A HYDROXYL GROUP ON THE REACTIVITY OF THE PARA-CARBONYL GROUP¹

BY LEO BRICKMAN², W. LINCOLN HAWKINS³, AND HAROLD HIBBERT⁴

Abstract

Attempts, by three independent methods of synthesis, to prepare vanilloyl acetaldehyde are described. In each case it has been shown that the presence of a para phenolic hydroxyl group either prevents or alters the normal course of the reactions. The synthesis of veratroyl acetaldehyde has been accomplished, and this product is described. A theoretical explanation for the mutual inter-relationship of the carbonyl and para phenolic hydroxyl group is suggested.

Introduction

Recent studies on the structure of lignin have resulted in the isolation of a large variety of compounds containing the guaiacyl and syringyl nuclei, in which a carbonyl group occupies a position para to the free phenolic hydroxyl group. Vanillin (22), guaiacol (13), and acetovanillone (5) have been isolated from the alkaline degradation products of lignin sulphonic acids obtained from soft woods, while similarly, from hard woods, these same products, along with their syringyl analogues, syringaldehyde (9), syringol (14), and acetosyringone (15), have been isolated.

Recently, a new series of lignin degradation products has been obtained from a variety of woods by the ethanolysis process (4, 6, 11). This method of converting lignin into simple building units consists in refluxing the resin-free wood meal with ethanolic hydrogen chloride in an inert atmosphere. The residual pulp is filtered off, and the solution, after concentration, poured into a large volume of water, from which the amorphous ethanol lignin precipitates out.

For many years the latter process was employed solely for the preparation of water-insoluble ethanol lignin, any soluble oils being entirely overlooked. A recent careful examination of the aqueous-ethanol filtrate from maple and other hard woods revealed the presence of an appreciable quantity of volatile oils (25 to 30%, based on the Klason lignin originally present). These crude oils were then separated into bisulphite-soluble, bicarbonate-soluble, alkali-soluble, and neutral fractions. In the case of spruce wood the yields were lower (10%), α -ethoxypropiovanillone (6) being isolated from the alkali fraction, and vanilloyl methyl ketone, along with vanillin, from the bisulphite

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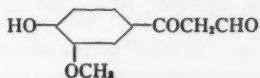
⁴ Professor of Industrial and Cellulose Chemistry.

fraction (3). Again, a chemical distinction between soft and hard woods was observed, hard woods yielding a mixture of the corresponding syringyl and guaiacyl derivatives. Thus, both α -ethoxypropiosyringone (11) and α -ethoxypropiovanillone were found to be components of the alkali fraction of maple, while syringaldehyde (20) and syringoyl methyl ketone (3), along with their guaiacyl analogues, were isolated from the bisulphite fraction.

Investigations in these laboratories, extending over several years, have resulted in a comprehensive study of this type of compound in which a carbonyl group occupies a position on the benzene nucleus para to a free hydroxyl group. The series of compounds that has been isolated from lignin offers a wide variety of such examples and includes aldehydes, methyl ketones, benzoin, and benzils. In every case, these lignin degradation products have been found to possess certain abnormal properties due, in general, to the presence of the free phenolic hydroxyl group. Thus vanillin, in contrast to a normal aromatic aldehyde, does not undergo the Cannizzaro reaction with alkalis, but on the contrary is stable for several hours to 8 *N* sodium hydroxide at 100° C. Furthermore, it has been observed that this abnormal stability disappears on replacement of the hydroxyl by an alkali-stable group such as methoxyl.

In the course of synthesizing several of these derivatives for identification purposes, further examples of this class of compound have been encountered. The presence of this free phenolic hydroxyl group in the para position to a carbonyl group has been found to influence both the rate and course of a variety of synthetic processes. In a study of the influence of solvents on the reactions of carbonyl compounds with the Grignard reagent, Lieff, Wright, and Hibbert (16) report the abnormal behaviour of vanillin and acetovanillone towards this reagent. In both cases, an apparent hindrance to normal addition at the carbonyl group was observed.

These preliminary observations indicated a mutual inhibiting effect on the reactivity of the carbonyl and phenolic hydroxyl groups when in the para position. In the present investigation, several attempts were made to synthesize vanilloyl acetaldehyde in order to compare its properties with those



Vanilloyl acetaldehyde

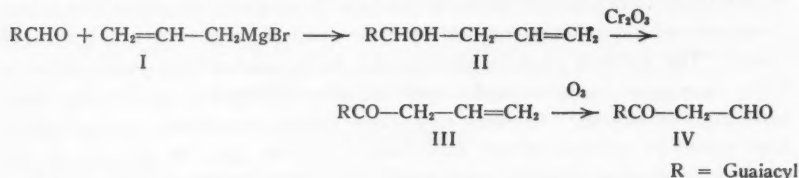
of one of the components of the ethanolysis bisulphite fraction from spruce and maple woods. All attempts to synthesize this substance were unsuccessful however, a fact attributable to the presence of the para phenolic hydroxyl in the various intermediates. It was therefore necessary to abandon this synthesis and to prepare the methylated derivative, veratroyl acetaldehyde, the synthesis of which proceeded smoothly and in good yield.

Discussion

The preparation of vanilloyl acetaldehyde was attempted by three independent methods of synthesis.

Synthesis (A).

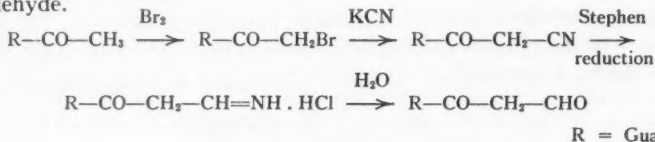
This was attempted by the action of allyl magnesium bromide on vanillin and its derivatives, the proposed synthesis involving the following steps:



With vanillin, the product obtained in the first step was an uncrystallizable yellow oil, the methoxyl analysis of which corresponded to the conjugated system, $\text{RCH}=\text{CH}-\text{CH}=\text{CH}_2$, presumably formed from the carbinol (II) by loss of water. To determine whether this secondary reaction was due to the influence of the free hydroxyl group, the methoxymethyl ether of vanillin was then treated similarly and a low yield of carbinol was obtained. Veratraldehyde, however, in which the phenolic hydroxyl is blocked by a more stable group, reacted smoothly to give a good yield of II which could be oxidized to III but not carried beyond this stage to give veratroyl acetaldehyde. This was probably due to the extreme sensitivity of veratroyl acetaldehyde to the reagents used to decompose the intermediary ozonide.

Synthesis (B).

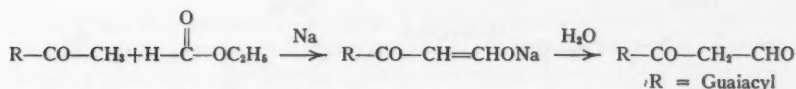
This method involved bromination of acetovanillone, conversion of the bromide to the nitrile, followed by a Stephen reduction (21) to give vanilloyl acetaldehyde.



With acetovanillone acetate as starting material, bromination was effected successfully and the resulting bromide converted to the nitrile. All attempts to reduce the nitrile by Stephen's method were unsuccessful.

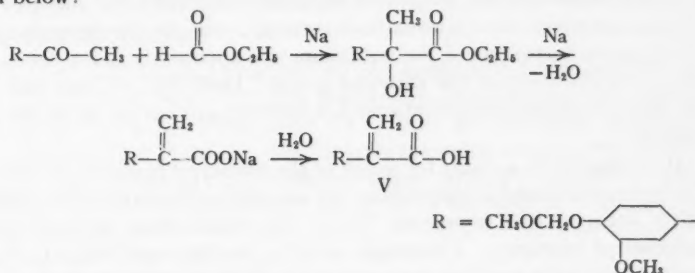
Synthesis (C).

This procedure involved a Claisen-Schmidt condensation of both acetovanillone and several of its derivatives with ethyl formate under the conditions used by Auwers (1, 2) to prepare benzoyl acetaldehyde.



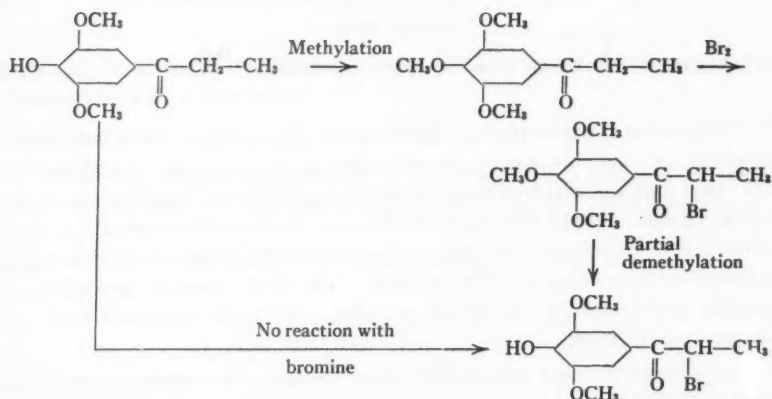
The influence of the para phenolic hydroxyl on the carbonyl group was apparent when acetovanillone was employed as the starting material. Condensation with ethyl formate, which depends on activation of the hydrogen atoms by the carbonyl group, did not take place in this case, acetovanillone being recovered unchanged. An attempt was then made to offset the influence of the phenolic hydroxyl by converting it to the acetate. The ester, however, proved to be unstable to the conditions of the reaction, and again acetovanillone was recovered unchanged.

Since methoxymethyl ethers have been shown to be relatively stable to alkali, the condensation was next attempted using the methoxymethyl ether of acetovanillone. In this instance a condensation was effected, but instead of the expected methoxymethyl ether of vanilloyl acetaldehyde a final reaction product that corresponded, in analysis and properties, to the methoxymethyl ether of α -guaiacyl acrylic acid (V) was obtained. It was possibly formed, as indicated below:



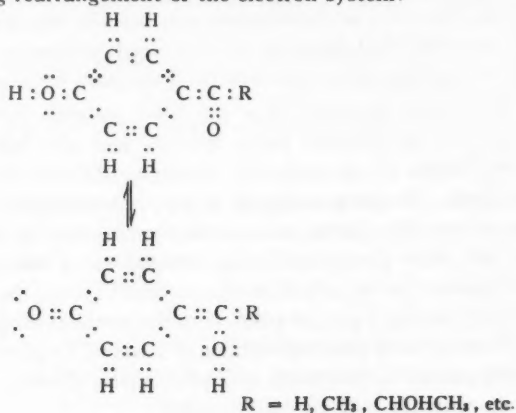
When, however, acetoveratrone was used in this condensation, a 90% yield of veratroyl acetaldehyde was obtained, indicating clearly the remarkable effect resulting from replacement of the para hydroxyl by a methoxyl group.

It is thus apparent that the para phenolic hydroxyl affects the reactivity of the carbonyl group directly and also influences the activation of other atoms in the molecule, rendering difficult the course of any reaction involving the para carbonyl group. Esterification seems to diminish the reactivity of the latter, or its ineffectiveness may be due to the ease of removal of the ester group under the conditions of the reaction. Etherification normalizes the behaviour of the carbonyl group, the methoxyl group, in this respect, having a greater effect than the methoxymethyl group. This fact is in agreement with the observations of Hunter, Cramer, and Hibbert (11), who, while unable to brominate propiosyringone directly, found this reaction took place normally with the methyl ether.



On the other hand, a number of observations have been made on the pronounced influence exerted by the carbonyl group on the reactions of a para phenolic hydroxyl group. Hunter and Hibbert (12) have shown that, whereas syringaldehyde, α -hydroxypropiosyringone, α -acetoxypropiosyringone and α -bromopropiosyringone, as well as propiosyringone, form a potassium salt with potassium acetate in ethanol solution, 3,5-dimethoxy-4-hydroxyphenyl propane (in which there is no carbonyl group) is completely unreactive towards this reagent, formation of the potassium salt apparently being dependent on the activating effect of the carbonyl group. Lock (17, 18) has also pointed out such interrelationships between 1,4-hydroxycarbinol groups in the benzene nucleus.

It is possible to account for many of the abnormal reactions of this class of 1,4-hydroxycarbonyl compounds on the assumption that a dynamic equilibrium exists between two resonating forms, this equilibrium shifting under the influence of reactants. This might be set up by the wandering of a hydrogen ion (proton) with resulting rearrangement of the electron system:



In this way it is possible to visualize a mutual interrelationship between the carbonyl and phenolic hydroxyl groups and to explain the resulting loss of activity in certain reactions, an explanation which, however, for the moment is a purely theoretical one.

Experimental

ATTEMPTED SYNTHESIS OF VANILLOYL ACETALDEHYDE

SYNTHESIS A. ACTION OF ALLYL MAGNESIUM BROMIDE

(I) On Vanillin

Allyl magnesium bromide was prepared according to the method of Gilman and McGlumphey (8). Vanillin (5 gm.) in anhydrous ether (70 cc.) was added to the Grignard reagent (2.5 moles) over a period of 30 min. with vigorous stirring. The mixture was allowed to stand overnight, decomposed with ice and dilute sulphuric acid, and then extracted with ether. The ethereal solution was extracted first with sodium bisulphite (20%) and then with sodium hydroxide (5%). The following fractions were obtained: (a) Bisulphite-soluble (vanillin), yield 2.88 gm.; (b) Alkali-soluble, yield, 1.7 gm.; (c) Residue, yield, 0.3 gm. The alkali-soluble fraction was a yellow oil distilling at a bath temperature of 160 to 220° C. at 0.01 mm. Found: OCH_3 , 17.7%. Calc. for $\text{C}_{11}\text{H}_{14}\text{O}_3$: OCH_3 , 16.0%.

(II) On Vanillin Benzoate

Vanillin benzoate (5 gm.) prepared by the method of Anderson (10) was treated with a slight excess of allyl magnesium bromide and the reaction mixture worked up as described under (I). There was recovered unchanged vanillin benzoate (2.1 gm.) and alkali-soluble material, presumably vanillin, (0.7 gm.). The experiment was repeated under varying conditions of time, temperature, and solvent but in all cases most of the original material was recovered unchanged.

(III) On Methoxymethyl Vanillin

This derivative was prepared according to the directions of Pauly and Wäscher (19). Methoxymethyl vanillin (25 gm.) was added to Grignard reagent (39.5 gm.) and the reaction mixture worked up in the usual manner. There was obtained α -allyl methoxymethyl vanillyl carbinol which was recrystallized from petroleum ether (b.p. 60 to 70° C.). Yield, 3.3 gm. (10%); m.p. 70 to 71° C.* Found: C, 65.2; H, 7.83; OCH_3 , 25.6%. Calc. for $\text{C}_{13}\text{H}_{18}\text{O}_4$: C, 65.5; H, 7.57; OCH_3 , 26.0%.

A portion of the product (1 gm.) was dissolved in acetone (5 cc.) and this solution added to potassium dichromate (0.5 gm.) dissolved in water (10 cc.) containing concentrated sulphuric acid (1 cc.). The temperature rose spontaneously to 70° C., the mixture at this point being very dark. After standing for 10 min., it was cooled and extracted with ether. Removal of the latter left 0.4 gm. of a brown resinous material that could not be crystallized nor distilled.

* All melting points are uncorrected.

(IV) On Veratric Aldehyde

Treatment of veratric aldehyde with allyl magnesium bromide gave α -allyl veratryl carbinol. Yield, 80%; m.p. 80.5 to 81.5° C. Found: C, 69.0; H, 7.5; OCH_3 , 29.9%. Calc. for $\text{C}_{12}\text{H}_{16}\text{O}_3$: C, 69.3; H, 7.7; OCH_3 , 29.8%.

Oxidation with chromic acid gave α -vinyl acetoveratrone which was recrystallized from ethanol-water followed by petroleum-ether (b.p. 60 to 70° C.). Yield, 50%; m.p. 58° C. Found: C, 69.7; H, 6.43; OCH_3 , 29.9%. Calc. for $\text{C}_{12}\text{H}_{14}\text{O}_3$: C, 69.8; H, 6.78; OCH_3 , 30.0%. The semicarbazone of the ketone was prepared and recrystallized from hot water; m.p., 140 to 142° C. Found: C, 59.2; H, 6.62; N, 16.2; OCH_3 , 23.5%. Calc. for $\text{C}_{13}\text{H}_{17}\text{O}_3\text{N}_3$: C, 59.3; H, 6.46; N, 16.0; OCH_3 , 23.6%.

Ozonization. α -Vinyl acetoveratrone (2.0 gm.), dissolved in glacial acetic acid (3 cc.), was cooled to 0° C. and ozone passed in until it was no longer absorbed. Calculation showed that this was a little in excess of theoretical. The ozonide was decomposed by the addition of ether (12 cc.) followed by zinc dust (1 gm.) and water (0.5 cc.). When the reaction had ceased, the solution was filtered, extracted with ether and the ethereal solution extracted first with bicarbonate and then with bisulphite, nothing dissolving in the latter. The ether residue was taken to dryness leaving a brown amorphous product no longer ether-soluble. A repetition with ethyl acetate as solvent gave the same result.

SYNTHESIS B. STEPHEN REDUCTION

(I) Of α -Cyanacetovanillone Acetate.

Preparation of α -Bromoacetovanillone Acetate. Acetovanillone acetate (10 gm.) was dissolved in anhydrous chloroform (75 cc.) and placed in a flask fitted with a stirrer, dropping funnel and reflux condenser. Bromine (7.8 gm.) in chloroform (25 cc.) was added slowly over a period of one and a half hours and the mixture then stirred for an additional hour. The chloroform solution was washed with water and bicarbonate, dried over sodium sulphate, and the solvent was removed under reduced pressure. A water-white liquid remained which solidified to colourless crystals on standing; yield, 12 gm. (87%). Recrystallization from ethanol gave a product melting at 86 to 87.5° C. Found: C, 46.0; H, 3.69; Br, 28.2; OCH_3 , 10.8%. Calc. for $\text{C}_{11}\text{H}_{11}\text{O}_4\text{Br}$: C, 46.0; H, 3.84; Br, 27.9; OCH_3 , 10.8%.

Preparation of α -Cyanacetovanillone Acetate. The procedure employed was that used by Gabriel (7) to synthesize α -cyanacetophenone. To a solution of 5 gm. of bromoacetovanillone acetate in ethanol (15 cc.) was added potassium cyanide (5 gm.) dissolved in water (15 cc.). The mixture was cooled, allowed to stand for 30 min., diluted with water (two volumes), and acidified with dilute hydrochloric acid. The heavy brown precipitate which separated out was removed by filtration and recrystallized from ethanol; yield, 1.3 gm. (32%); m.p. 191 to 192° C. Found: C, 62.0; H, 4.80; N, 6.2; OCH_3 , 13.2%. Calc. for $\text{C}_{12}\text{H}_{11}\text{O}_4\text{N}$: C, 61.8; H, 4.72; N, 6.0; OCH_3 , 13.3%.

Stephen Reduction of α -Cyanacetovanillone Acetate. Anhydrous stannous chloride (1.2 gm.) was placed in a flask with anhydrous ether (25 cc.) and saturated with anhydrous hydrogen chloride. The nitrile (0.97 gm.), which was insoluble in ether and chloroform, was suspended in chloroform and added to the ether solution with vigorous shaking. After shaking for two hours, the reaction mixture was filtered, and 0.9 gm. of unchanged α -cyanacetovanillone acetate recovered.

(II) Of α -Cyanacetovanillone

Deacetylation of α -Bromoacetovanillone Acetate. α -Bromoacetovanillone acetate (10 gm.) was dissolved in methanol (100 cc.) containing concentrated hydrochloric acid (10 cc.). The solution was heated to boiling point, allowed to stand three hours and then cooled to -10°C . A crop of colourless crystals melting at 102 to 103°C . was obtained; yield, 7.0 gm. (88%). Analysis showed that not only had the acetate group been removed but that bromine had been replaced by chlorine. Found: C, 53.8; H, 4.61; Cl, 17.9; OCH_3 , 15.3%. Calc. for $\text{C}_9\text{H}_9\text{O}_3\text{Cl}$: C, 53.8; H, 4.48; Cl, 17.7; OCH_3 , 15.5%.

Preparation of α -Cyanacetovanillone. This derivative was prepared directly by bromination of acetovanillone acetate followed by treatment of the deacetylated bromide with potassium cyanide. Yield, 23%; m.p. 152 to 153°C . Found: C, 62.9; H, 4.66; N, 7.05; OCH_3 , 16.2%. Calc. for $\text{C}_{10}\text{H}_9\text{O}_3\text{N}$: C, 62.8; H, 4.71; N, 7.33; OCH_3 , 16.2%. Several attempts were made to reduce this compound in the manner already described, but were unsuccessful. Removal of the acetyl group did not increase the solubility of the nitrile in cold organic solvents.

SYNTHESIS C. CLAISEN-SCHMIDT CONDENSATION

(I) Condensation of Acetovanillone Acetate with Ethyl Formate.

A mixture of acetovanillone acetate (2.2 gm.) and ethyl formate (1.32 gm.), dissolved in benzene (3 cc.), was added to sodium wire (0.28 gm.) suspended in anhydrous benzene (7 cc.). A vigorous reaction ensued which slowed down as the sodium became coated with the reaction product. After standing 12 hr., the precipitate was filtered off, washed with ether and dried in the air; yield 0.95 gm. The product was dissolved in water (5 cc.), acidified with dilute sulphuric acid, extracted with ether, and the ether removed. The solid residue was recrystallized from water; it melted at 112 to 114°C . A mixed melting point with acetovanillone showed no depression.

(II) Condensation of Methoxymethyl Acetovanillone with Ethyl Formate.

Preparation of Methoxymethyl Acetovanillone. This was prepared in the same way as the corresponding ether of vanillin, except that the time of shaking was cut to 30 min. The product was recrystallized from petroleum ether (b.p. 60 to 70°C .); yield, 52%; m.p. 52 to 53°C . Found: C, 62.4; H, 6.34; OCH_3 , 29.4%. Calc. for $\text{C}_{11}\text{H}_{14}\text{O}_4$: C, 62.9; H, 6.66; OCH_3 , 29.5%.

Claisen-Schmidt Condensation. This was carried out in the manner already described. The reaction product was recrystallized from petroleum ether (b.p. 60 to 70° C.); m.p. 58 to 59° C. It gave no reaction with semicarbazide acetate or 2,4-dinitrophenyl hydrazine hydrochloride, indicating the absence of a carbonyl group. It decolorized bromine in carbon tetrachloride and permanganate in acetone, proving the presence of an unsaturated bond. It did not react with *p*-nitrobenzoyl chloride, showing the absence of a free hydroxyl group. Finally, it dissolved in bicarbonate with the evolution of carbon dioxide, indicating the presence of a carboxyl group. These properties, coupled with the analytical data, correspond with those of the methoxymethyl ether of α -guaiacyl acrylic acid. Found: C, 60.3; H, 5.82; OCH₃, 25.9%. Calc. for C₁₂H₁₄O₅: C, 60.5; H, 5.88; OCH₃, 26.0%.

(III) Condensation of Acetoveratrone with Ethyl Formate

Synthesis of Veratroyl Acetaldehyde. A mixture of acetoveratrone (12 gm., prepared by methylating acetovanillone with dimethyl sulphate) and ethyl formate (7.5 gm.) was added to sodium wire (1.5 gm.) in benzene (40 cc.). After standing 12 hr., the reaction product was filtered off and dried in the air; yield 12 gm. (90% calculated as veratroyl acetaldehyde).

A portion of this sodium salt (4 gm.) was dissolved in water (10 cc.), acidified with dilute sulphuric acid, and extracted with ether. Removal of the solvent left a reddish oil (3 gm.) which on distillation (bath temperature 180 to 230° C. at 0.1 mm.) gave a clear yellow oil; yield, 0.9 gm. Most of the aldehyde polymerized during the distillation. Found: C, 63.6; H, 5.84; OCH₃, 30.1%. Calc. for C₁₁H₁₂O₄: C, 63.5; H, 5.76; OCH₃, 29.8%.

Preparation of the Copper Salt. Veratroyl acetaldehyde (0.15 gm.) was dissolved in a small amount of ether and shaken with a saturated aqueous solution of copper acetate. A green crystalline precipitate immediately settled out; it was filtered, washed with ether and water, and dried; yield, 0.12 gm. Found: C, 55.0; H, 4.79; OCH₃, 25.9%. Calc. for C₂₂H₂₂O₈Cu: C, 55.25; H, 4.60; OCH₃, 25.35%.

Preparation of the Semicarbazone. The sodium salt of veratroyl acetaldehyde was treated with semicarbazide hydrochloride in water, and the precipitate formed was filtered off and recrystallized from ethanol; m.p. 181 to 182° C. Found: C, 54.2; H, 5.94; N, 15.9; OCH₃, 23.5%. Calc. for C₁₂H₁₅O₄N₃: C, 54.35; H, 5.66; N, 15.8; OCH₃, 23.4%.

Preparation of the 2,4-Dinitrophenylhydrazine. To the free aldehyde dissolved in water was added an excess of 0.4% of 2,4-dinitrophenylhydrazine hydrochloride in water. The precipitate which formed was filtered off and recrystallized from chloroform-petroleum ether (b.p. 30 to 50° C.) and then dioxane-petroleum ether (b.p. 30 to 50° C.); m.p. 189 to 190° C. Found: C, 52.3; H, 4.4; N, 14.4; OCH₃, 16.05%. Calc. for C₁₇H₁₆O₇N₄: C, 52.5; H, 4.12; N, 14.4; OCH₃, 15.95%.

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A NEW SOURCE OF COCOSITOL¹BY RICHARD H. F. MANSKE²

Abstract

The leaves of *Calycanthus floridus* and of *C. glaucus* have been shown to contain a polyhydric alcohol, $C_6H_{12}O_6$, which has been identified as cocositol.

The name cocositol was given by Müller (1) to a polyhydric alcohol that he isolated from the leaves of two plants belonging to the natural family Arecaceae (Palmaceae), namely, *Cocos nucifera* and *C. plumosa*. Analytical figures and molecular weight data pointed unmistakably to the simple formula, $C_6H_{12}O_6$, and this was confirmed by the preparation of a normal hexa-acetate. That it was an optical isomer of inositol seemed highly probable because the nitric acid oxidation product yielded a pink coloured compound with calcium chloride (Scherer reaction). Müller pointed out that his cocositol was probably identical with a substance, quercin, obtained by Vincent and Delachanal (2) from some quercitol mother liquors prepared from acorns.

The author has obtained a substance from the leaves of *Calycanthus floridus* and from *C. glaucus* (Calycanthaceae) that has proved to be identical with cocositol in all respects save one. Müller records that cocositol is optically inactive. The substance now isolated is slightly but measurably dextro-rotatory, namely $[\alpha]_D^{24} + 1.6^\circ$ ($c = 0.4$ in. water). Cocositol as now obtained melts sharply and without decomposition at $367^\circ \text{C}.$ * The melt on slight cooling recrystallizes immediately. If a specimen is heated cautiously over a free flame on a platinum spatula it melts to a colourless liquid that crystallizes at once when withdrawn from the heat. Müller had considerable difficulty in determining such a high melting point and records 345 to $350^\circ \text{C}.$ uncorrected. On the author's uncorrected thermometer it melted at $354^\circ \text{C}.$ The hexa-acetate was recrystallized from boiling acetic anhydride, and it melted sharply at $302^\circ \text{C}.$ with no trace of discoloration or decomposition. When cooled to $301^\circ \text{C}.$ it crystallized again. This melting and cooling was repeated some ten times without changing the melting point. Müller records $300^\circ \text{C}.$ (corr.) for the melting point of the acetate.

Cocositol (as also the author's compound) dissolves in warm sulphuric acid without coloration and it crystallizes unchanged from hot concentrated nitric acid. The inositol colour reaction depending on nitric acid oxidation

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² Chemist.

*All melting points are corrected.

is therefore difficult to get with cocositol, but repeated evaporation with nitric acid ultimately yields enough croconic acid to give a colour with calcium chloride. With lead sub-acetate it yields a heavy precipitate.

Inasmuch as an authentic specimen of cocositol was not available for direct comparison, Prof. J. E. Hawley of the Department of Mineralogy, Queen's University, Kingston, Ontario, has kindly carried out a crystallographic study of the author's compound and its acetate. Müller records such a study as carried out by Prof. T. V. Barker and the following table completely confirms the identity of the two pairs of substances.

Polyhydric Alcohol—Submitted by R. H. F. Manske	
Crystallography	J.E.H.
Crystals—Monoclinic, slightly distorted	Monoclinic
$m : m - 110 \wedge \bar{1}10 = 64^\circ 9'$ (2-circle goniometer measurement)	$110 \wedge \bar{1}10 = 64^\circ 18' - 64^\circ 9'$
Measured with Contact Goniometer on one large crystal	Mean
$\beta = 117^\circ +$	$\beta = 117^\circ 12'$
$110 \wedge \bar{1}11 = 58^\circ \pm$	$110 \wedge \bar{1}11 = 57^\circ 56'$
$\bar{1}10 \wedge \bar{1}11 = 60^\circ \pm$	$\bar{1}10 \wedge \bar{1}11 = 59^\circ 56'$
Forms present—prisms (110)	110
hemi-pyramids ($\bar{1}11$)	$\bar{1}11$
hemi-orthodome (201)	201
Basal pinacoid (001)	001
Crystal habit similar to drawings by Barker	
J.E.H.	
Optical Properties—Biaxial, Positive (+)	Barker
Extinction on 110 = 34° (average).....	33°
Maximum extinction measured against elongation = 38°	
Indices of refraction	
α or $N_p = 1.550 \pm .002$	
β or $N_m = 1.560 \pm .002$	
γ or $N_o = 1.615 \pm .002$	
Birefringence $\pm .06$ Extreme	Strong (but not measured quantitatively)
Optic plane \perp to 010 at $92^\circ 42'$ to (001) c	One of mean lines (x , y , or z) is almost perpendicular to c (001)
Trace of optic plane \wedge (001) c , measured on prismatic section = $92^\circ 42'$	
No marked dispersion of optic axes	
Acetate of Polyhydric Alcohol or Cocositol	
Crystallography	J.E.H.
Probably monoclinic, positive data not obtained on account small-sized crystals	Monoclinic
Forms on crystallites [110] [001]	[110] [001] forms as illustrated
Additional form on larger crystals is probably a hemi-orthodome	Not described
Angles measured on petrographic microscope	Goniometer
CM : $001 \wedge 110 = 84^\circ 18' \pm$	$001 \wedge 110 = 84^\circ 26'$
$\beta = 98^\circ \pm$	$\beta = 97^\circ 33'$
Habit—near cubic	Habit—near cubic
No cleavage	No cleavage

Optical Properties—Biaxial—negative (—)

Extinction on $m = 29^\circ - 35^\circ$ 33°Maximum extinction measured against elongation = 44° Prism faces (m) give near centered optic axis figure Prism faces (m) give near centered optic axis figure

Indices of refraction

$$\alpha = 1.48 \pm .003$$

$$\beta = 1.51 \pm .003$$

 $\gamma > 1.51$ (not obtainable from grains)Birefringence $\pm .04$ (medium) Medium

No marked dispersion of optic axes

(Y or N_m) Elongation on prism section = $16^\circ - 17^\circ$

It may be added that a flavone-like compound of undetermined identity was also obtained from the leaves.

Experimental

The leaves of *Calycanthus floridus* and of *Calycanthus glaucus* were collected, in the autumn when the vegetative period was virtually complete, from shrubs growing in the Arboretum, Central Experimental Farm, Ottawa. The author is indebted to Mr. John Adams for permission to collect them.

The dried and ground materials were separately extracted with hot methanol during which extraction a sparingly soluble substance separated in crystalline form from the extract. After several weeks the extract was filtered and the crystals washed with methanol and then with acetone. The insoluble portion was next extracted with hot water and the filtered solution evaporated to dryness on a steam bath. The resulting residue was recrystallized twice from hot water with the aid of charcoal and then washed with methanol. The brilliant colourless prisms thus obtained melted sharply and without decomposition at 367°C . The yield of purified cocositol from either source was slightly more than 0.5%. Calc. for $\text{C}_6\text{H}_{12}\text{O}_6$; C, 40.00; H, 6.67%. Found: C, 40.00, 40.00; H, 6.84, 6.79%. The optical activity was found to be $[\alpha]_D^{24} + 1.6^\circ$ ($c = 0.4$ in. water).

Cocositol Hexa-acetate

The purified cocositol was suspended in 100 times its weight of acetic anhydride containing a little pyridine and an equal weight of anhydrous sodium acetate. The mixture was boiled under reflux until the solid had completely dissolved (24 to 48 hr.). On cooling the mixture, cocositol hexa-acetate crystallized in large colourless prisms that were filtered off and washed with water and then with methanol. It then melted at 301 to 302°C . It was redissolved in boiling acetic anhydride (75 cc. of solvent per gram of substance) and the solution filtered through a crucible with a sintered glass plate heated by being suspended in the vapour of boiling acetic anhydride. The filtered solution was evaporated until crystallization began in the boiling liquid. After cooling, the brilliant colourless crystals were filtered off and washed with methanol, water, and methanol in the order named. The

substance then melted sharply and without discoloration or decomposition at 302° C., the melt crystallizing when it was allowed to cool to 301° C. Calc. for $C_{18}H_{24}O_{12}$; C, 50.00; H, 5.56%. Found: C, 50.10, 50.12; H, 5.76, 5.73%.

Isolation of a Flavone (?)

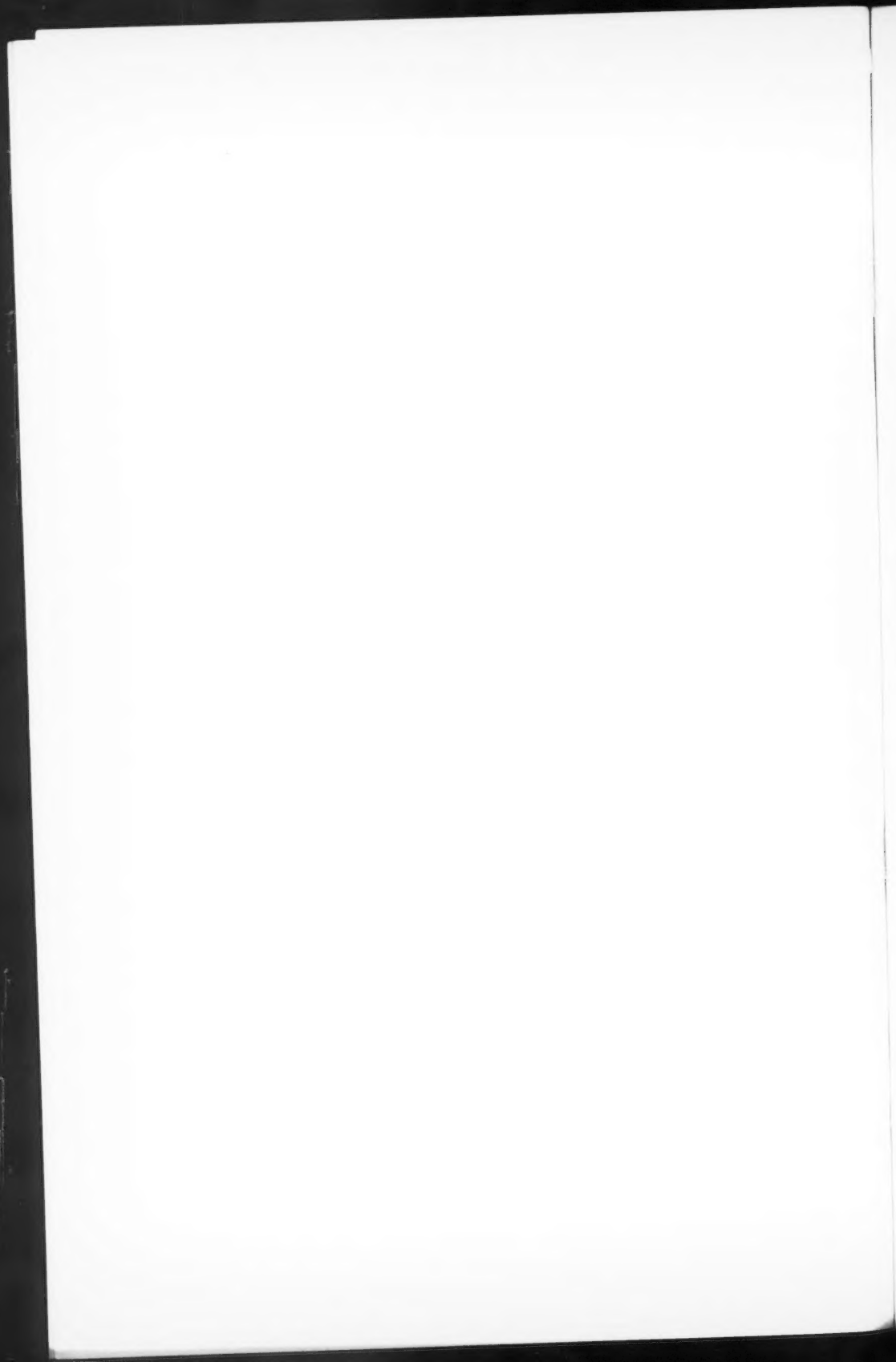
The methanolic filtrate from which the cocositol had crystallized was evaporated to a thick syrup, diluted with hot dilute hydrochloric acid, and the remainder of the methanol boiled out. After several days the mixture was filtered and the clear filtrate extracted repeatedly with ether. The residue from the combined ether extracts was triturated with water and the crystalline substance thus obtained filtered and washed with water. It was recrystallized twice from methanol-water (70 : 30) and obtained in pale yellow fine needles melting at 296° C. Calc. for $C_{18}H_{10}O_6 \cdot H_2O$; C, 59.21; H, 3.95%. Found: C, 58.90, 58.91; H, 3.92, 3.94%. Methoxyl was absent.

References

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2. VINCENT, C. and DELACHANAL. Compt. rend. 104 : 1885. 1887.







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